Historical Data Review of Dissolved Oxygen and Related Parameters for the Lavaca Bay TMDL Project

Christine Ritter, Post Doctoral Assistant
Paul A. Montagna, Professor
Marc Russell, Graduate Research Assistant
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Christine Ritter,

Paul A. Montagna, and

Marc Russell

University of Texas at Austin

Marine Science Institute

750 Channel View Drive

Port Aransas, TX 78373

Historical Data Review Report to:

Texas Natural Resource Conservation Commission

12100 Park 35 Circle

Austin, TX 78753

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Introduction

This historical data review is part of the Lavaca Bay/Chocolate Bay (Segment 2453) Total Maximum Daily Load (TMDL) Project. The data generated will be used to identify areas within the segment for further investigation, assess the segment for Dissolved Oxygen (DO) exceedences, and support the development of a TMDL for DO. Segment 2453 was listed on the 305(b) list because DO concentrations are occasionally lower than the criterion established to assure optimum conditions for aquatic life in a 13.7-square mile area near the Alcoa Ship channel.

"Aquatic life use" is a term used in Texas water resource management to characterize water bodies and specify water quality criteria for those bodies. The Texas Natural Resource Conservation Commission (TNRCC) has identified four aquatic life use categories: exceptional, high, intermediate, and limited. The TNRCC criteria for DO varies with the Aquatic life use designation of a water body (Table 1; Texas Natural Resource Conservation Commission, 2000). For Texas estuaries designated with exceptional aquatic life use, DO criteria are 24-hr mean < 5.0 mg l^{-1} and 24-hr minimum < 4.0 mg l^{-1}. Lavaca Bay (segment 2453) is designated for exceptional aquatic life use. Estuaries designated for high aquatic use must meet less strenuous criteria of 24-hr mean < 4.0 mg l^{-1} and 24-hr minimum < 3.0 mg l^{-1}.

Dissolved oxygen is a parameter used to evaluate aquatic ecosystem health. Dissolved oxygen is a useful indicator because it is required for organism respiration and microbial sediment decomposition processes (Strobel and Heltshe 2000). In addition, low DO (i.e., hypoxia) can be caused by excess nutrient inputs into the aquatic system (e.g., sewage outfalls, non-point source pollution, etc.).

Table 1: Aquatic life use categories with dissolved oxygen criteria and attributes describing each category (copied from Texas Surface Water Qaulity Standards, 2000).

Aquatic Life Use	Dissolved Oxygen Criteria, mg/L			Aquatic Life Attributes					
	Freshwater mean/ minimum	Freshwater in Spring mean/ minimum	Saltwater mean/ minimum	Habitat Characteristics	Species Assemblage	Sensitive Species	Diversity	Species Richness	Trophic Structure
Exceptional	6.0/4.0	6.0/5.0	5.0/4.0	Outstanding natural variability	Exceptional or unusual	Abundant	Exceptionally high	Exceptionally high	Balanced
High	5.0/3.0	5.5/4.5	4.0/3.0	Highly diverse	Usual association of regionally expected species	Present	High	High	Balanced to slightly imbalanced
Intermediate	4.0/3.0	5.0/4.0	3.0/2.0	Moderately diverse	Some expected species	Very low in abundance	Moderate	Moderate	Moderately balanced
Limited	3.0/2.0	4.0/3.0		Uniform	Most regionally expected species absent	Absent	Low	Low	Severely imbalanced

In the scientific literature, low oxygen is referred to as hypoxia and is typically defined as occurring when instantaneous (or grab sample) measurements of DO are < 2 mg O_2 l^{-1} (Ritter and Montagna 1999). Other common definitions in the scientific literature are < 2 ppm (Dauer et al. 1993) and < 2 ml O_2 l^{-1} (Diaz and Rosenberg 1995). Hypoxic conditions create stress on biotic communities, and can lead to reduction in populations and biomass of aerobic organisms.

Although the presence of hypoxia is typically used as an indicator of water quality in scientific papers, it is not used as a regulatory indicator. A variety of standards for low oxygen criteria exist, each developed to fit the specific mission of the regulatory agency and that agency's sampling program. The TNRCC has established DO criteria based on 24-hr average DO that varies with the aquatic life designation of a water body (Table 1; Texas Natural Resource Conservation Commission, 2000). For Lavaca and Chocolate Bays (Segment 2453), the criteria for exceptional aquatic life require minimum 24-hr DO measurements to be greater than 4 mg/L and average 24-hr DO measurements to be greater than 5 mg/L. If these criteria are not met, the measurements are called exceedences and could be listed as impaired.

The goal of this historical data review is to compile 24-hr DO data available for assessment, assess the occurrence of low DO based on TNRCC criteria, and identify how DO values vary temporally and spatially for future study within Lavaca Bay/Chocolate Bay (segment 2453). Should a TMDL be necessary, information is needed for other parameters as well. Salinity and temperature, and water depth affect the solubility of DO in estuarine waters. Salinity and temperature can vary with depth, and there is often a correlation between depressed DO values and higher bottom salinity in estuaries. Dissolved oxygen concentration is a result of processes that consume and produce it. These processes are often controlled by nutrient quantities. Thus, nutrient data is also analyzed in this review.

Dissolved Oxygen Dynamics

Dissolved oxygen concentration in an aquatic ecosystem is a function of biotic (living) and abiotic (non-living) components. Major biotic components include photosynthesis, the production of sugars and other organic molecules by photoautotrophs using the energy from sunlight, and respiration, the breakdown of these same molecules by heterotrophs for energy (Fig. 1). A byproduct of photosynthesis is the production of O_2 while respiration requires the consumption of O_2 to harness chemical bond energy. Abiotic components have both direct and indirect effects on dissolved oxygen concentrations. Temperature, salinity, and pressure all affect the solubility of oxygen in water. A driving force of the ecosystem, photosynthesis, is limited by nutrients in the water. Combining major biotic and abiotic components yields a highly dynamic picture of dissolved oxygen concentrations over space and time.

Aquatic plants and animals live in a more dynamic environment compared to their terrestrial relatives who enjoy a relatively stable 20% concentration of O_2 in the air. Phytoplankton, photosynthetic organisms in the water column, may have insufficient light because they live in a turbid water column (Ragotzkie, 1960). Phytoplankton must have enough sunlight to have a photosynthetic rate above their respiration rate in order for them to have net production

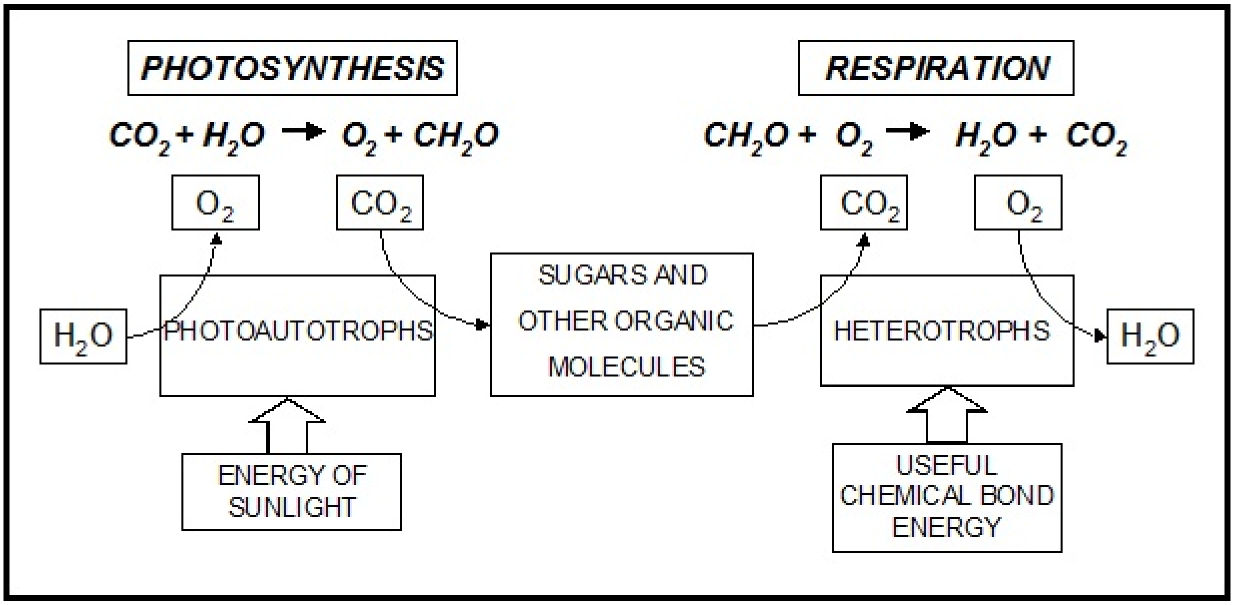


Figure 1: Major biological pathways of photosynthesis and respiration. Photosynthesis uses energy from sunlight to produce sugars and other organic molecules. These molecules in turn serve as food for other organisms.

of O_2. If non-photosynthetic organisms, located in the same water column, are using more O_2 than the net production of their photosynthetic counterparts there will be a decrease in the dissolved oxygen present in that part of the water column. The position in the water column, and subsequent light intensities, are not static like in terrestrial environments but change as a result of dynamic abiotic factors.

Highly dynamic aquatic environments are a result of changes and gradients that take place over varied time and space scales. Interfaces at the surface and at the benthos represent areas that have large gradients over small spatial scales. These interfaces dictate how much oxygen moves into and out of the water column. The water-atmosphere interface is the site of transfer of O_2 from its' gaseous state in the air to its' dissolved state in the water. The more turbulent this interface is the deeper bubbles of air will be forced. Henry's Law predicts that as a bubble travels into deeper waters increasing pressure will cause more gas to dissolve in the water. Turbulence also plays an indirect role in dissolved oxygen concentrations by causing vertical mixing of organisms in shallow waters. Vertical mixing can take place at different rates depending on things such as wind speed over the surface and degree of stratification of the water column. The movement of O_2 (dQ/dt, mg/m/hr) across the water-atmosphere interface is given by
$dQ/dt = A(D)(1/dz)(C-C_s)$, where A is the surface area, dz is the thickness of the hypothetical film separating gas and liquid, D is the molecular diffusivity, and C is the aqueous gas concentration. The term dz is inversely proportional to water turbulence and wind speed (Day et al, 1989). The sediment-water interface is the site of O_2 transfer to and from the benthic organisms and the water column. If sunlight penetrates to the bottom then photosynthetic

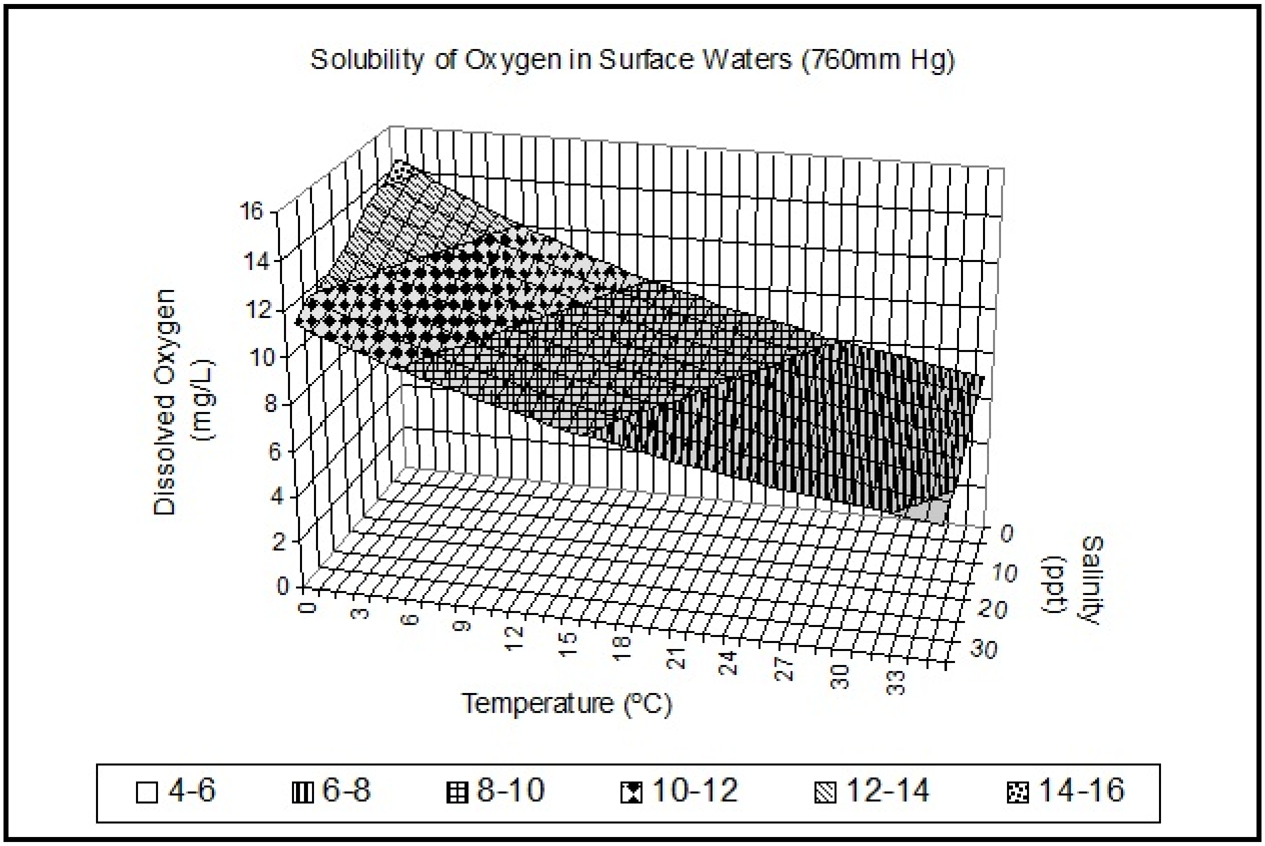


Figure 2: Interaction between temperature and salinity on dissolved oxygen (graph developed from data compiled by Colt, 1984).

benthic organisms such as micro-algae and sea grasses may produce excess dissolved oxygen. These organisms usually inhabit a very thin layer of surface sediment under which dissolved oxygen concentrations decline to zero as it is used by organisms within the sediments (Fenchel and Riedl, 1970). The majority of sediments are thus devoid of oxygen, a condition termed anoxic.

Larger scale gradients and longer time span components also affect dissolved oxygen concentrations in estuaries. Temperature affects the solubility of gases in aquatic media, and is dynamic from hourly to geologic time scales. Temperature has an indirect relationship with the solubility of gas in a liquid (Fig. 2). Relatively shallow waters heated by the summer sun can become so hot that their dissolved oxygen content becomes dangerously low for aquatic life during the night-time when community respiration is greater than photosynthesis (Park et al., 1958). Salinity, the concentration of salts in the water, interacts with temperature to dictate the solubility of oxygen. This makes fresh water and oceanic water flux another very important abiotic factor. Aquatic environments not only flow vertically, which brings organisms from the surface to the benthos, but also flow horizontally. Large fresh water fluxes into an aquatic environment from direct precipitation or from stream flow, for example, can bring with it waters

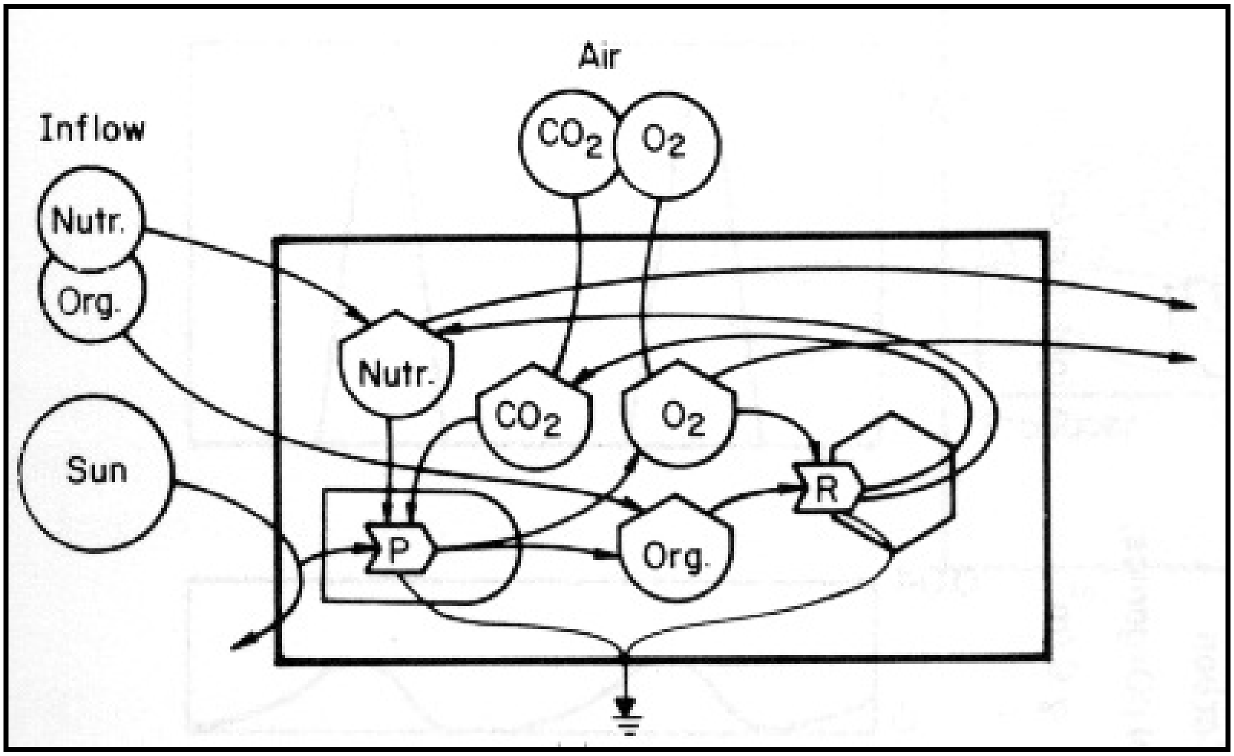


Figure 3: Ecosystem model of oxygen dynamics in an estuary. Nutrients (Nutr.) from inflow are a direct limiting factor on photosynthesis (P) and an indirect limiting factor on the production of dissolved oxygen (O_2) (Odum, 1983).

relatively high in dissolved oxygen. Horizontal flows from fresh water or oceanic waters also have an indirect effect on dissolved oxygen by displacing the organisms normally associated with a water body. If the above fresh water example flushes into a coastal region such as an estuary, the organisms needing higher salinities will be displaced by lower salinity tolerant species (Welsh et al, 1972). These organisms will produce or consume more dissolved oxygen. Pressure has a direct relationship with the solubility of oxygen in water. Pressure change is an example of a mesoscale gradient. The values presented in Figure 2 are only valid at the surface of the water column, which has a pressure of 760 mm Hg. Increases in depth cause the pressure to increase around a bubble of air, and more oxygen is forced into solution. This manifests itself as an upward shift of the area in Figure 2. Temperature, salinity, and pressure interact over varying time and space scales, which result in a highly dynamic physical environment.

At the ecosystem level, photosynthesis is limited primarily by the amount of available nutrients (Fig. 3). In estuarine systems, the limiting nutrient is often nitrogen (Thayer, 1974). Nitrogen enters estuarine systems via streams, rivers, or runoff from the land. Characteristics of watersheds and climatic influences regulate nutrient loading rates. Anthropogenic nutrient sources can be large in some estuaries adjacent to areas with high population densities or high

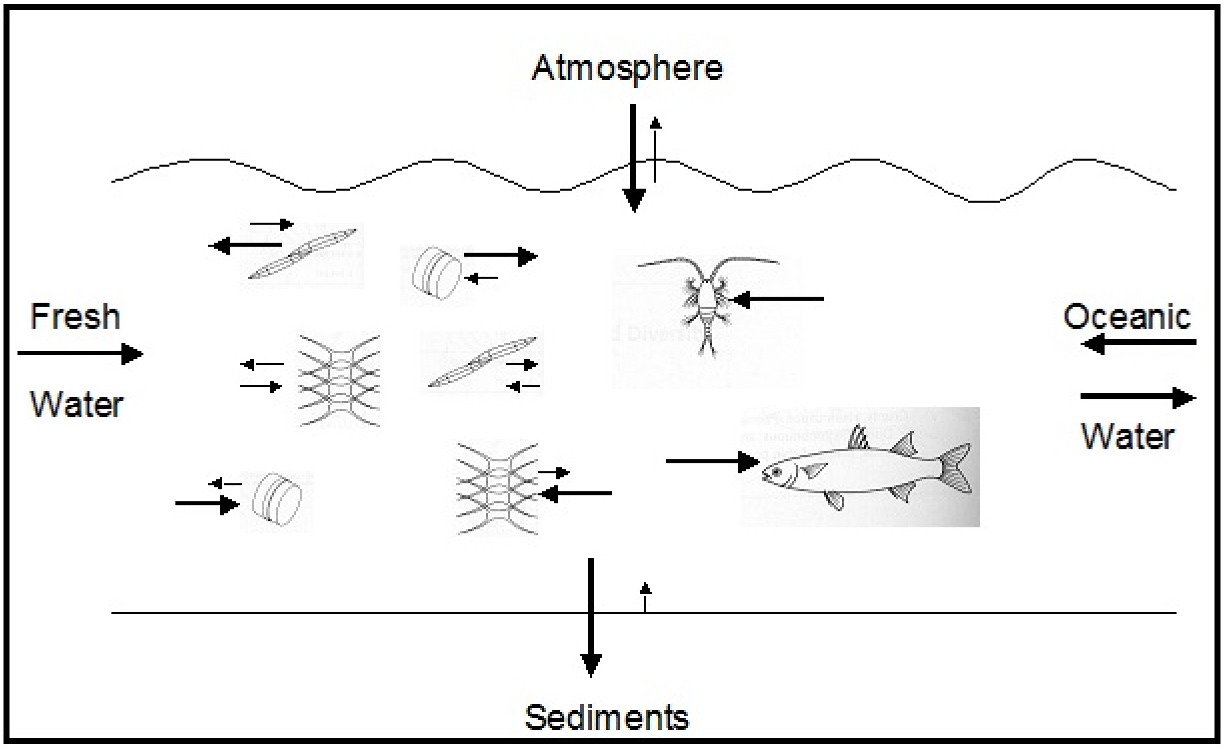


Figure 4: Movements of dissolved oxygen in an aquatic ecosystem based on biotic and abiotic components. Sizes of arrows indicate the relative flux of dissolved oxygen.

intensity agriculture. Nutrients are constantly cycling between organic and inorganic forms because of biological uptake and regeneration. Thus, nutrient concentration and speciation dynamics can control dissolved oxygen concentrations

Circulation and mixing in estuaries are spatially and temporally dynamic. Stratification is variable and ephemeral (Ritter and Montagna, 1999) so concentrations of nutrients (e.g. nitrate, nitrite, and ammonia) change dramatically with depth. Stratification can result in rapidly increasing ammonia concentrations with increasing depth (Webb and D'Elia, 1980). Dissolved oxygen concentration can decrease below the stratification barrier. Estuaries can change from well mixed to stratified and back again in less than two days or stratification can last through entire seasons. During extended periods of stratification, dissolved oxygen concentrations can become dangerously low in deeper waters (Rabalais and Turner, 2001). The net result is that stratification dynamics can be an important factor controlling dissolved oxygen concentrations.

Interactions between biotic and abiotic components that regulate dissolved oxygen are highly dynamic spatially and temporally (Fig. 4). Photosynthesis and respiration, the two main biotic components, are influenced by many abiotic factors. Vertical mixing will cycle photoautotrophs from high intensity light at the surface to low intensity light near the benthos. Turbidity of the water regulates the degree of attenuation of light as it travels through the water column.

Horizontal flow can displace volumes of water and their biotic inhabitants. Nutrient uptake and regeneration cycles take place on different spatial and temporal scales. Temperature, salinity, and pressure changes have direct influences on dissolved oxygen concentrations in water.

Diurnal, seasonal, and geologic climatic events influence the rates of many of these abiotic and biotic processes. An understanding of estuarine dissolved oxygen dynamics must include all of these components.

Methods

Unitization

Dissolved oxygen is expressed in a variety of units. The preffered unit is mg/L, which is mass per unit volume of a liquid. At 20 ‰ salinity, 25 °C temperature, and 1 atmosphere pressure, a DO concentration of 1 mg/L = 1 ppm = 0.7 ml/L = 32 μM = 62.5 μg at/L = 3% O_2 by volume = 14% saturation (Diaz et al. 1992).

Datasets

Data for all the parameters that will be measured in field sampling for the Lavaca Bay TMDL Project were requested from the TNRCC on January 24 2002, however, data was available for only 22 of the 41 requested parameters. Parameters for which data from segment 2453 were obtained are listed in Table 2. Data obtained covered the period 16 July 1969 to 13 November 2001. Stations for which data were available are plotted in Figure 5. Most TNRCC hydrographic measurements were from grab samples; grab samples are samples, or composite samples (i.e., depth profiles) taken at a single point in time. The data forwarded by the TNRCC also contained minimum 24-hr DO and average 24-hr DO data; 24-hr average DO is calculated as the average DO over a continuous 24-hr period and 24-hr minimum DO is the minimum DO over the same 24-hr period (Appendix A; DO Fact Sheet).

Two TNRCC datasets (event and results) for Segment 2453 were merged by TAGID and Enddate and then transposed using SAS statistical software to create a matrix with samples as rows and variables (i.e., parameters) as columns. The Tag ID is a variable name used by the TNRCC to combine the two datasets. The only problem encountered was that several duplicates in the dataset were found that prevented transposition. Each of these potential duplicates was examined individually to determine if it was a duplicate or a replicate. All were clearly duplicates being that they were the same value for the same date and station. All duplicates were deleted from the dataset. Following merging and transposition, each storet code, which identifies a variable, was represented in its own column.

24-hr DO data was culled from the dataset and supplemented with additional 24-hr data obtained from TNRCC field staff but not yet available as of this writing via TNRCC headquarters. This dataset was used to evaluate the availability of data for the DO assessment at the end of this project.

Table 2: Parameters for which Lavaca Bay/Chocolate Bay (Segment 2453) data was requested from TNRCC. Parameters for which data was available for segment 2453 is marked with a ✔. Avg. = average, min. = minimum, max. = maximum.

Parameter	Units	Storet	Data Available for Segment 2453
24-hr number of observations	no units	89858	✔
24-hr avg. DO	mg/L	89857	✔
24-hr min. DO	mg/L	89855	✔
24-hr max DO	mg/L	89856	✔
24-hr avg. Conductivity	uS/cm	00212	
24-hr min. Conductivity	uS/cm	00214	
24-hr max. Conductivity	uS/cm	00213	
24-hr avg. Salinity	‰	00218	
24-hr min. Salinity	‰	00219	
24-hr max. Salinity	‰	00217	
24-hr avg. Temperature	°C	00209	
24-hr min. Temperature	°C	00211	
24-hr max. Temperature	°C	00210	
Avg. Water Depth	m	89862	
DO	mg/L	00300	✔
Conductivity	uS/cm	00094	✔
Salinity	‰	00480	✔
Temperature	°C	00010	✔
Cholorphyll *a*	mg/L	13855	✔
Total Water Depth	m	82903	
Days Since Last Significant Rainfall	days	72053	✔
Sediment TOC	mg/kg	81951	✔
Sediment C	g/kg	00696	
Sediment N	mg/kg	00603	
Sediment Clay Content	% dry wt	82009	✔
Sediment Silt Content	% dry wt	82008	✔
Sediment Sand Content	% dry wt	89991	✔
Sediment Gravel Content	% dry wt	80256	✔
Biological Reporting Units	NA	89899	✔
Benthic Sampler	NA	89946	✔
Diversity (H′)	NA	90020	
Equitability (J′)	NA	90025	
Total number of Species in Sample	NA	90034	
Benthos Sampled - No Organisms Present	NA	90037	
Total Nitrogen Ammonia	mg/L	00610	✔
o-phosphorus	mg/L	00671	✔
nitrate+nitrite	mg/L	00631	✔
silicate	mg/L	00958	
Chlorophyll-*a*	ug/L	32211	✔
Biological Oxygen Demand	mg/L	00310	✔
Chemical Oxygen Demand	mg/L	00340	✔

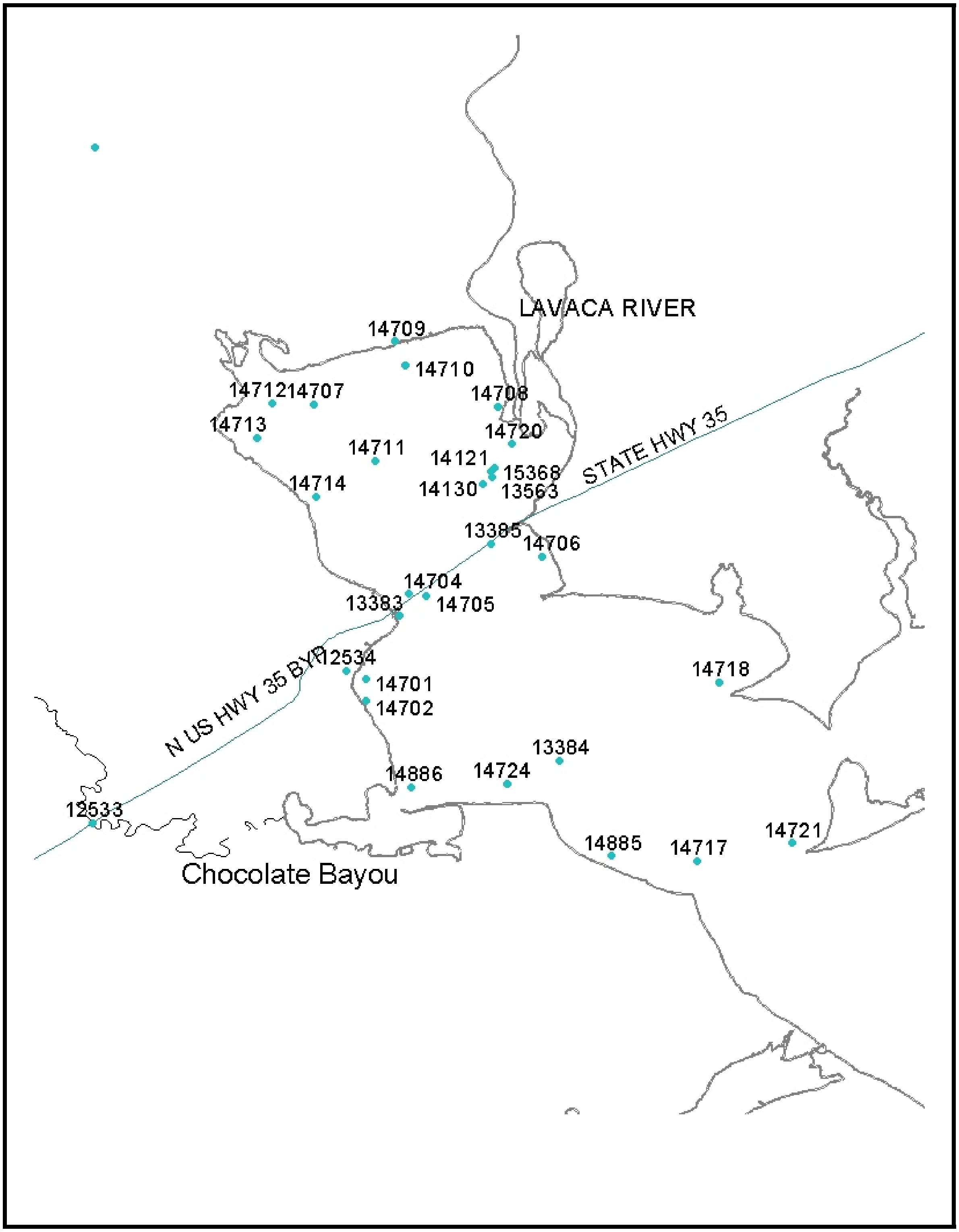


Figure 5: Map of TNRCC stations in Segment 2453 according to locations of record. Stations 13383 and 13385 are not denoted at the locations TNRCC field personnel say they sample.

Analysis of Hydrographic and Nutrient Characteristics

The transposed dataset was used to assess the occurrence of DO < 5 mg/L, DO < 4 mg/L, and DO < 2 mg/L. A second dataset was created from the transposed matrix by extracting data taken at a depth of 0.4 m or less. Extracting data of depth < 0.4 m ensured that depth profile data was omitted from analysis. It also ensured that data included in the analysis was within the depth region where DO data is required to be collected by the Surface Water Quality Monitoring (SWQM) Procedures Manual.

Frequency analysis of DO, conductivity, salinity, temperature, ammonia, ortho-phosphate, nitrate+nitrite, chlorophyll *a,* and biological oxygen demand (BOD) was conducted for all stations within segment 2453 using the second dataset. In addition, frequency analysis was conducted for DO by station for those stations with more than 25 observations at a depth of 0.4 m or less. A total of 12 stations were analyzed.

Conservative mixing diagrams, which plot nutrients as a function of salinity, were created using the second dataset for ammonia and ortho-phosphate. There was not enough nitrate+nitrite data to yield a meaningful diagram. These diagrams are used to identify ecological processes affecting nutrients in estuaries.

A third dataset was created from the transposed matrix by limiting the dataset to surface observations (i.e., < 0.4 m). Parameter values were plotted by Julian date so that seasonal trends might be noted. This dataset was also used to evaluate DO exceedences, and for station analyses.
Of 35 stations for which DO data was available in segment 2453, DO was examined in detail at only 5 stations: 13384, 13385, 13383, 12534, and 13563. These stations were chosen because 1) they had the most DO data, 2) they had recent DO data, and/or 3) they had low DO observations. Selected depth profiles obtained from the transposed matrix were plotted for DO and salinity at each station to assess the degree of stratification and the possible relationship between stratification and low oxygen. Of these 5 stations, continuous 24-hr DO data was available for only stations: 13383, 13384, and 13385, because TNRCC only recently implemented a new method for assessing DO based on 24-hr measurements.

For each of the five stations, SigmaSal and SigmaDO were calculated for all observations for which depth profile data was available for both DO and salinity. SigmaSal = $\text{Salinity}_{\text{bottom}}$ - $\text{Salinity}_{\text{surface}}$. SigmaSal is an indicator of salinity stratification; a positive SigmaSal value indicates higher salinity in bottom water. SigmaDO = $\text{DO}_{\text{bottom}}$ - $\text{DO}_{\text{surface}}$. SigmaDO is an indicator of benthic DO depression; a negative SigmaDO value indicates lower oxygen in bottom water. Frequency and cumulative frequency distributions were plotted for SigmaSal and SigmaDO to assess the frequency of large disparities between surface and bottom values for salinity and DO. In addition, coincident SigmaSal and SigmaDO were plotted and linear regression was conducted to assess the relationship between stratification and oxygen depletion. The line used to model SigmaSal and SigmaDO data was: SigmaDO = a + b * SigmaSal, where a and b were coefficients fit to the data.

Analysis of Non-TNRCC Data

Grab-sample data available from Formosa, Alcoa, the University of Texas Marine Science Institute (UTMSI), and Texas Parks and Wildlife Department (TPWD) are summarized in the results section. 24-hr DO data was available only from the Texas Water Development Board (TWDB). TWDB and TPWD conduct a joint ambient water quality monitoring program by which DO is monitored continuously for roughly one month. This data was downloaded from the internet: http://hyper20.twdb.state.tx.us/data/bays_estuaries/datasonde/Lavaca/. Only the first 24 hours of each deployment was used in this review to be consistent with the TNRCC QA requirements for DO data reporting (see Appendix A). 24-hr average, minimum, and maximum were determined for each observation. These datasets were reviewed separately and none of the data was included in the review of TNRCC's dataset. Each dataset was collected under a QAPP.

Results

Julian Analysis

Of the parameters plotted over the Julian year, only water temperature (Fig. 6a) and DO (Fig. 6d) demonstrated a seasonal trend. Water temperature increased during the summer, whereas DO decreased during the summer. No discernable trend was found for ammonia, nitrate+nitrite, or ortho-phosphate (Figs. 7a, 7b, and 7c) for which values were mostly < 1 mg/L. Chlorophyll *a* (Fig. 7d) may have a summer signature, but there are only a few observations indicating such a relationship.

Analysis of Surface Observations

The distribution of surface, grab-sample DO values (Fig. 8) follows a normal distribution. Roughly 77% of observed values fall within the range of 5 - 10 mg/L. More than 90% of the observations are below 10 mg/L. Dissolved oxygen values ranged 1 - 14.35 mg/L.

The distribution of conductivity values (Fig. 9) is bi-modal and skewed toward lower values of conductivity. Roughly 42% of conductivity observations were less than 6000 uS/cm. The remaining observations are roughly normally distributed between 6000 - 54000 uS/cm.

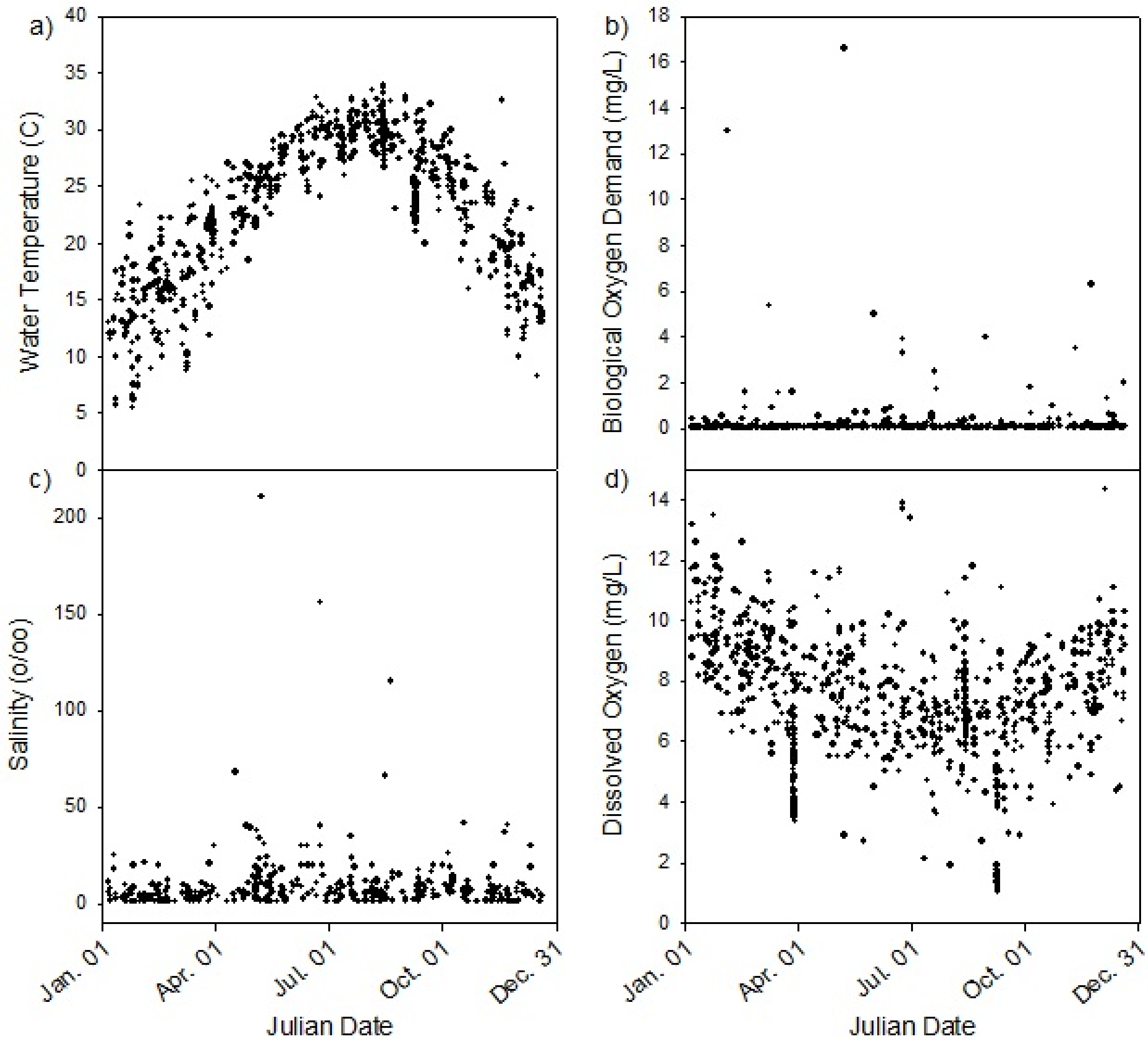


Figure 6: Parameter values plotted by the julian day of the year. a) Water temperature, b) biological oxygen demand, 3) salinity, and d) dissolved oxygen.

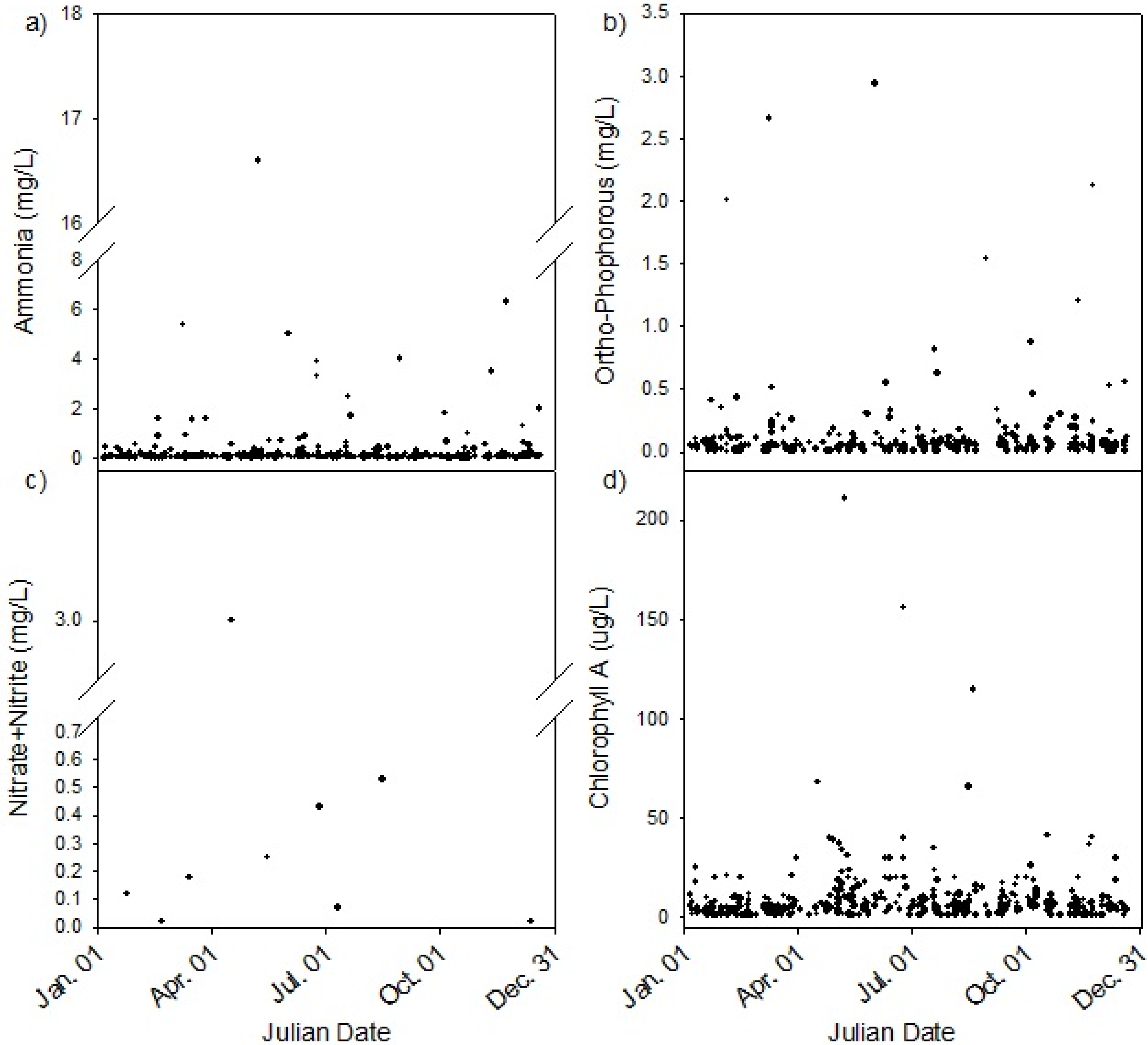


Figure 7: Parameter values plotted by the julian day of the year. a) ammonia, 2) ortho-phosphate, 3) nitrate+nitrite, and 4) chlorophyll *a*.

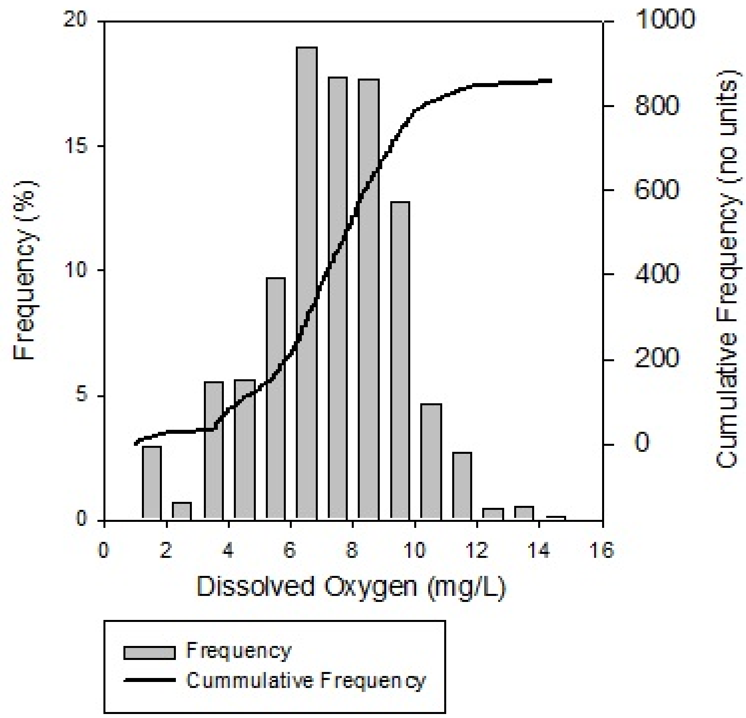


Figure 8: Frequency of dissolved oxgyen values (mg/L). N = 856, mean = 7.24, std. dev. = 2.23, min. = 1.00, and max. = 14.35.

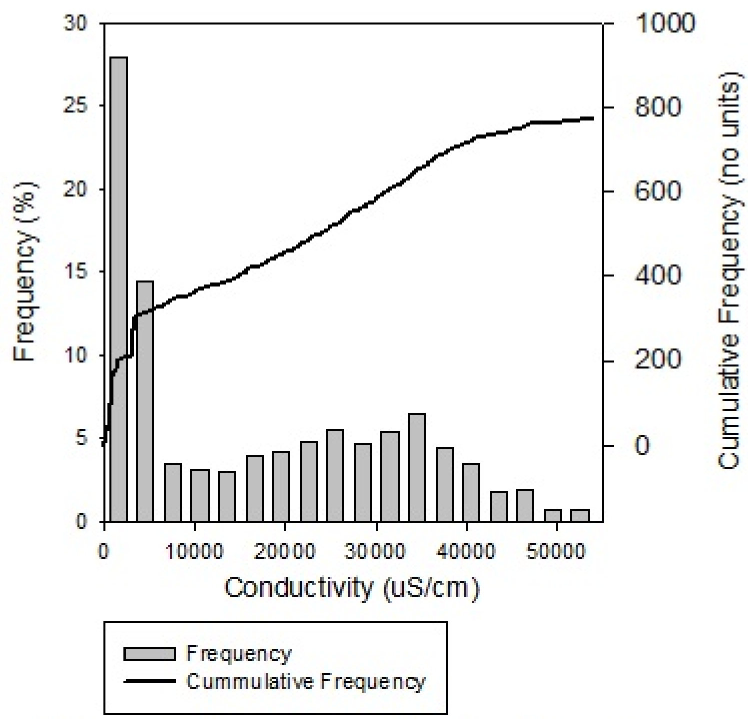


Figure 9: Frequency of conductivity values (uS/cm). N = 771, mean = 16310, std. dev. = 15081, min. = 55, and max. = 53900.

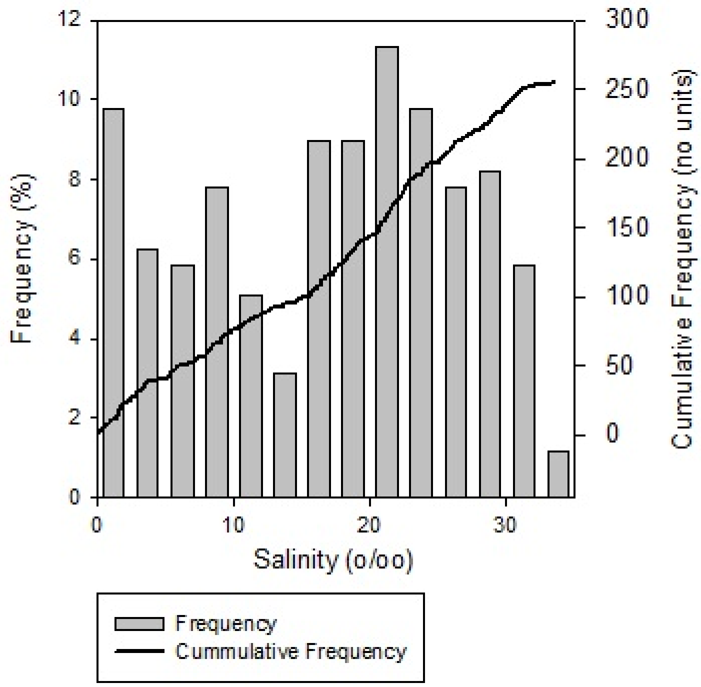


Figure 10: Frequency of salinity values (o/oo). N = 256, mean = 16.77, std. dev. = 9.45, min. = 0, and max. = 33.5.

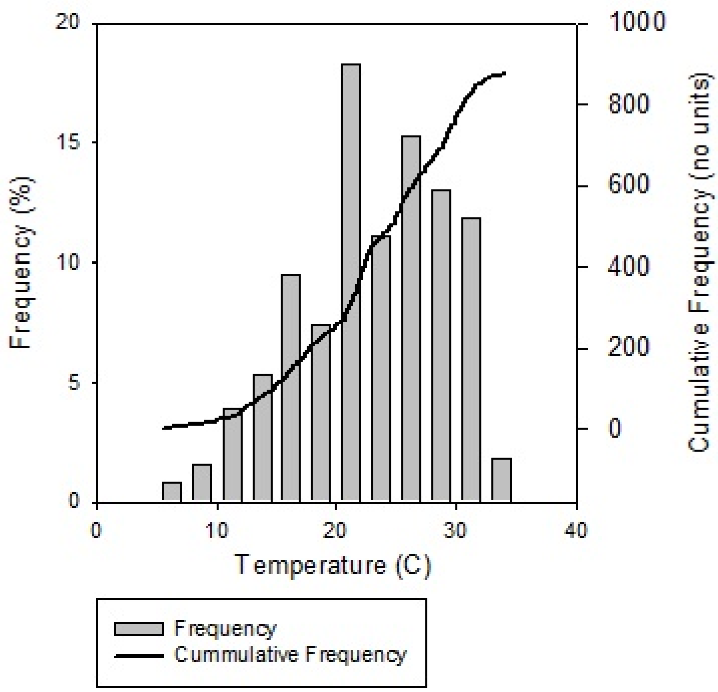


Figure 11: Frequency of temperature values (C). N = 875, mean = 22.82, std. dev. = 6.08, min. = 5.50, and max. = 33.97.

The distribution of salinity values (Fig. 10) appears to be bimodal though the plot of cumulative frequency indicates a normal distribution. The distribution peaks at 0 - 2.5 ‰ and 20 - 22.5 ‰. Only 7% of the observations are greater than 30 ‰, and roughly 30% of the values are lower than 10 ‰.

Water temperature ranged between 5.5 and 34.0 °C (Fig. 11). The distribution is skewed to the right; 71% of the values are higher than 20 °C.

Ammonia values ranged between 0.01 and 16.6 mg/L (Fig. 12a). The distribution is skewed to the left with 96% of the values being less than 1 mg/L. Of note are the outlier values that are clear indicators of nutrient enrichment, which could contribute to DO depletion. Of 426 observations, more than 59% are less than 0.08 mg/L (Fig. 12b). The distribution of data peaked at between 0.04 and 0.06 mg/L with 25% of observations falling in this range.

Ortho-phosphate values ranged between 0.002 and 2.941 mg/L (Fig 13a). The distribution was skewed to the left with 96% of the observations being < 0.5 mg/L and 25% being < 0.02 mg/L.

Very few observations of nitrate+nitrite were available for analysis. As with the other nutrient distribution, nitrate+nitrite distribution appears to be skewed left. Of the 9 observations, 1 was > 3 mg/L, and the remaining 8 were < 1mg/L (Fig. 14).

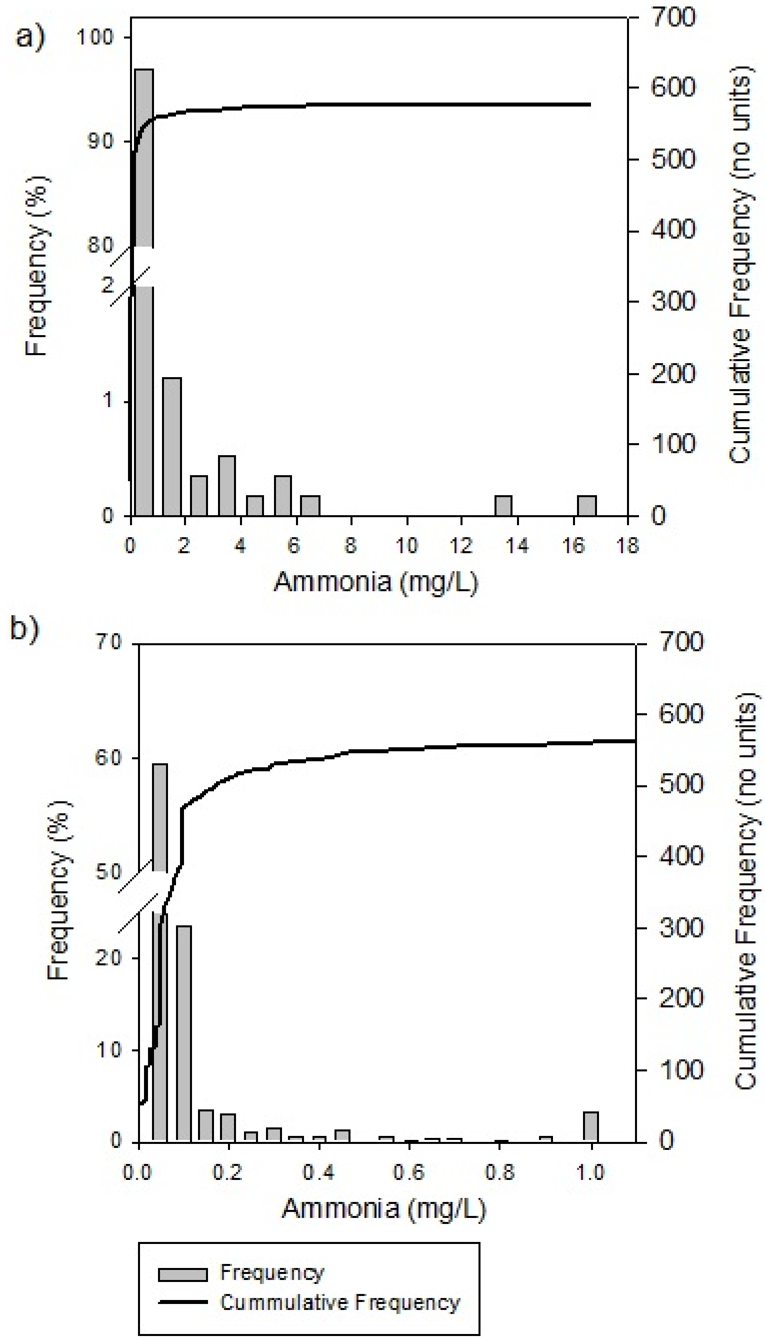


Figure 12: Frequency of ammonia values (mg/L). N = 582, mean = 0.22, std. dev. = 1.02, min. = 0.01, and max. = 16.6. a) covers the range 0 - 18 mg/L. b) covers the range 0 - 1 mg/L. Note: all values > 1.0 mg/L are lumped into thelast category.

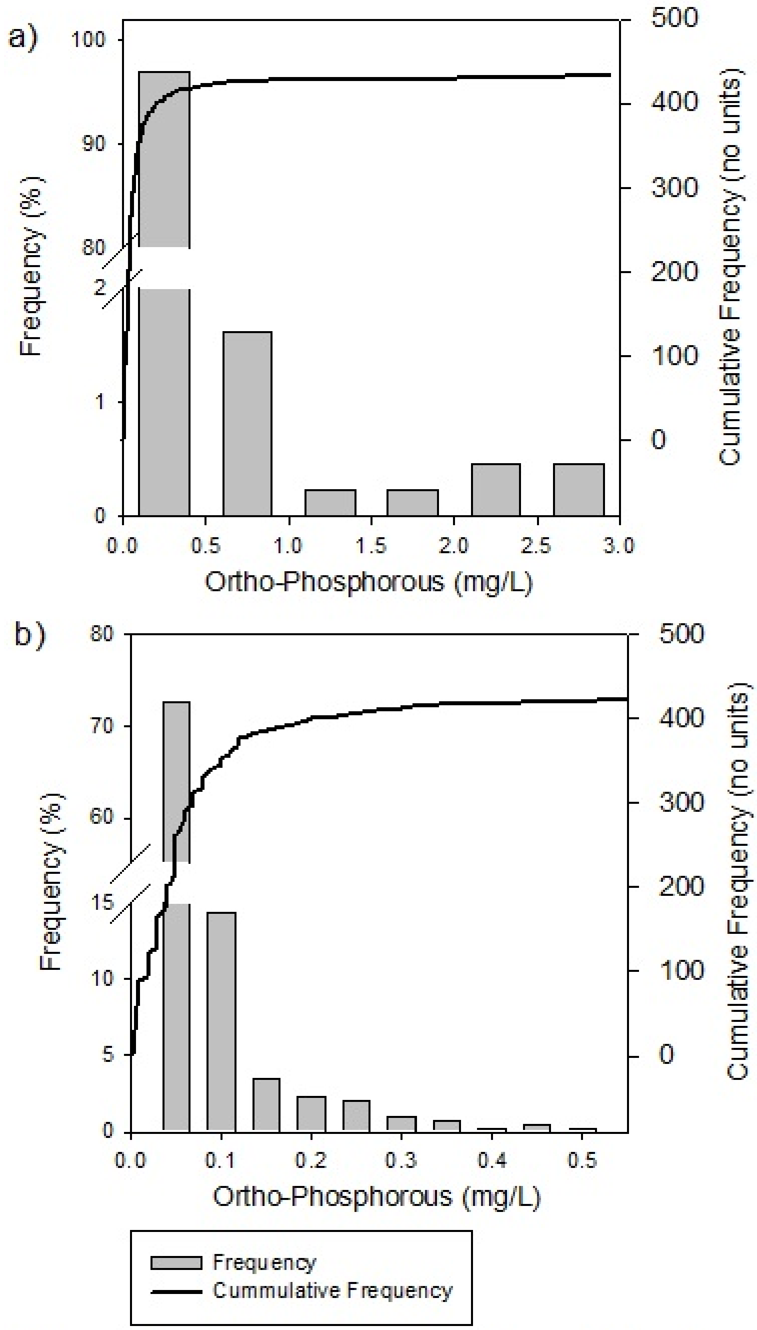


Figure 13: Frequency of ortho-phosphate values (mg/L). N = 452, mean = 0.098, std. dev. = 0.260, min. = 0.002, and max. = 2.941. a) covers the range 0 - 3 mg/L. b) covers the range 0 - 0.55 mg/L. Note: all values > 0.55 mg/L are lumped into the final category.

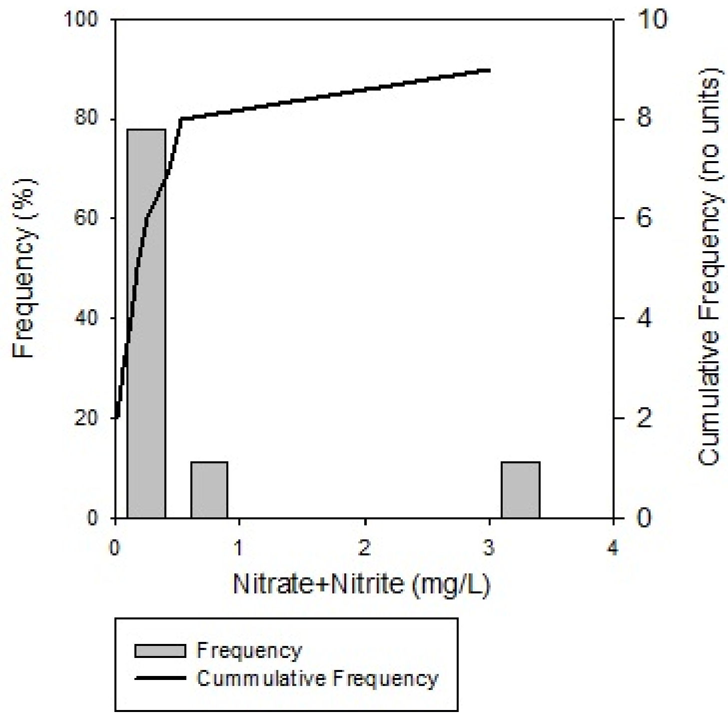


Figure 14: Frequency of nitrate+nitrite values (mg/L). N = 9, mean = 0.51, std. dev. = 0.95, min. = 0.02, and max. = 3.00.

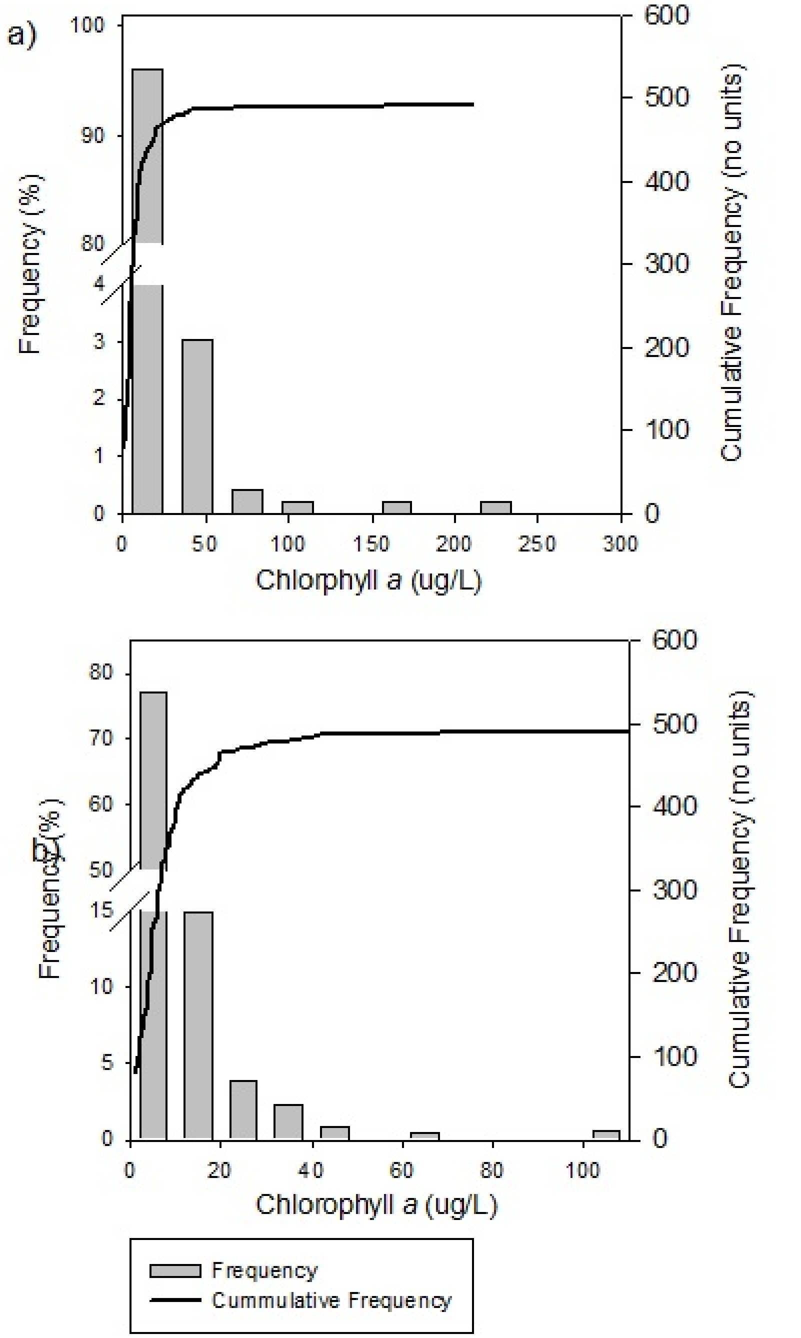


Figure 15: Frequency of chlorophyll *a* values (ug/L). N = 496, mean = 8.27, std. dev. = 14.66, min. = 1, and max. = 211. a) covers the range 0 - 300 ug/L. b) covers the range 0 - 110 ug/L. Note: All values > 110 ug/L are lumped into the final category.

Chlorophyll *a* values ranged between 1 and 211 ug/L. The distribution of observations was skewed left with 94% of the observations being < 30 ug/L (Fig. 15a) and 74% being < 10 ug/L (Fig. 15b).

Biological oxygen demand (BOD) was measured using 5-day, 20 °C incubations. The range of BOD values was 0.5 to 16.0 mg/L (Fig. 16). The distribution of BOD values was skewed left, peaking between 1 and 2 mg/L. However, four outlier values were higher than 8, and one was as high as 16 mg/L.

Higher nutrient concentrations are associated with lower salinities (Fig. 17). Conservative mixing diagrams for ammonia and ortho-phosphate indicate that the Lavaca Bay estuary is a net sink for nutrients.

<u>Station Analyses</u>

Dissolved oxygen data was available for 35 stations in segment 2453. Of these, 13 stations had at least one DO observation < 5 mg/L, and seven stations had a DO observation < 4 mg/L (Table 3; these values do not represent exceedences because they are based on grab-sample data). Five stations had at least one DO observation < 2 mg/L, the commonly accepted definition of hypoxia (Table 4). Stations 13385 and 13384 have the most frequent occurrence of hypoxia.

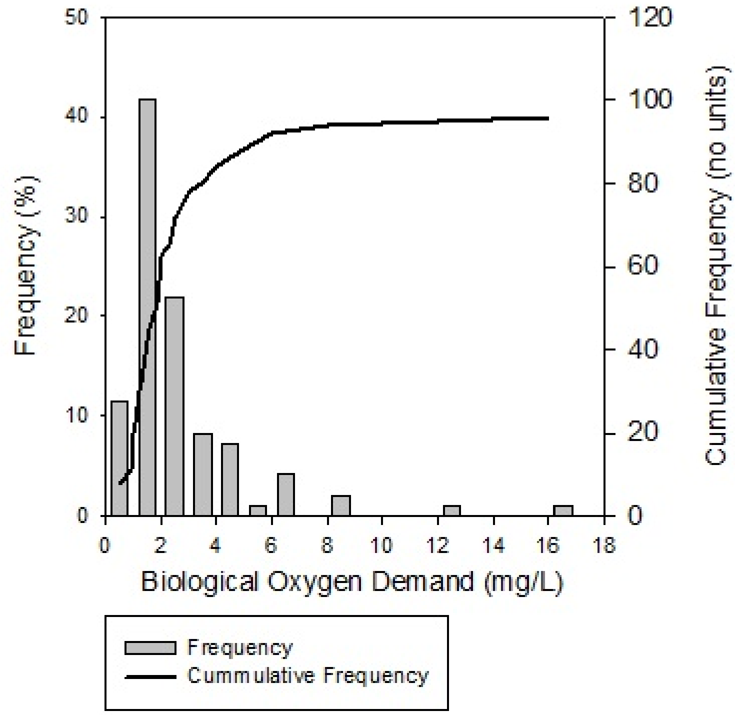


Figure 16: Frequency of biological oxygen demand values (mg/L). N = 96, mean = 2.44, std. dev. = 2.33, min. = 0.5, and max. = 16.0. BOD was measured using 5-day, 20 °C incubations.

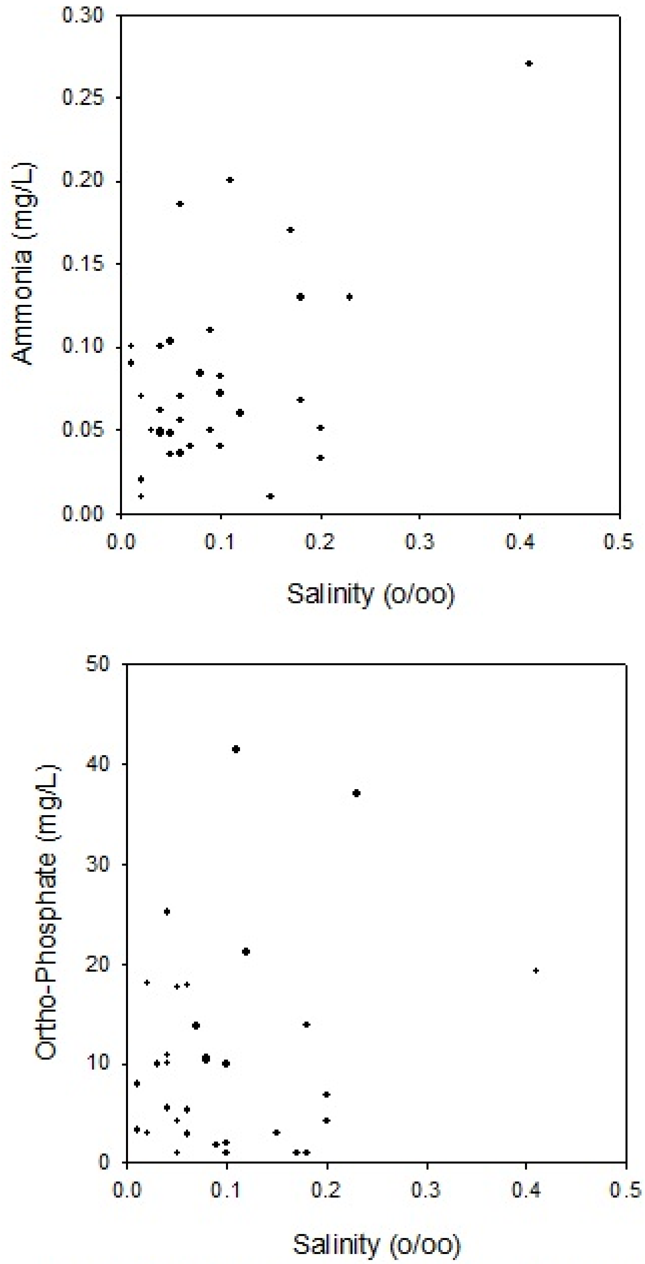


Figure 17: Conservative mixing diagrams for a) ammonia and b) ortho-phosphate.

Table 3: Number of observations at each station indicative of low oxygen during the period 16 July 1969 to 13 November 2001. Stations with no dissolved oxygen (DO) data have been omitted. Station = TNRCC station ID. N = total number of DO observations. Observations based on grab-sample data; 24-hr time series and depth profile data are considered as single observations.

Station	N	Number of observations where DO < 5 mg/L	Number of observations where DO < 4 mg/L
12533	27	1	-
12534	62	17	9
13288	9	4	4
13289	50	7	5
13290	2	-	-
13291	54	2	-
13292	2	-	-
13294	4	1	-
13295	17	5	3
13383	154	4	1
13384	128	36	17
13385	100	49	33
13563	30	1	-
14701	2	-	-
14702	5	-	-
14703	4	-	-
14704	6	-	-
14705	5	-	-
14706	2	-	-
14707	6	-	-
14708	4	-	-
14709	4	-	-
14710	6	-	-
14711	5	-	-
14712	5	-	-
14713	5	-	-
14714	6	-	-
14717	3	-	-
14718	4	-	-
14720	49	1	-
14721	4	-	-
14724	4	-	-
14885	4	-	-
14886	5	-	-
15368	24	1	-

Table 4: Number of observations, at each station with low DO (i.e., DO < 5 mg/L; Table 3), that had hypoxic observations (i.e., DO < 2 mg/L). Station = TNRCC station ID. N = total number of DO observations. Observations based on grab-sample data; 24-hr time series and depth profile data are considered as single observations.

Station ID	N	Hypoxia
		# DO observation < 2 mg/L
12533	27	-
12534	62	4
13288	9	1
13289	50	1
13290	2	-
13291	54	-
13292	2	-
13294	4	-
13295	17	-
13383	154	-
13384	128	7
13385	100	17
14720	49	-
15368	24	-

The distribution of surface (depth < 0.4 m) grab-sample observations were roughly normal for 11 of the 12 stations chosen for DO frequency analysis (Figs. 18 and 19). Station 13288 was skewed left with 50% of the observations below 5 mg/L. Only 2 stations did not have any observations < 5 mg/L: 14720, and 15368 (Figs. 18 and 19). Two stations had surface observations that were hypoxic (i.e., < 2 mg/L): 12534 and 13288 (Fig. 18).

STATION 13385

At station 13385, water column stratification is not season specific (Figs. 20 and 21). Stratification was not observed during January, March and December, but this may be an artifact of data limitations during those months. In cases where salinity stratification occurred, DO concentrations declined, sometimes below 2 mg/L (e.g., February 1998, May 1995, July 1998, August 1995).

The distribution of SigmaSal values (Fig. 22) is skewed to the left. Approximately 28% of SigmaSal observations were ≤ 2 ‰ (Fig. 22), leaving the remaining 72% to be indicative of salinity stratification.

The distribution of SigmaDO values is skewed slightly to the right (Fig. 23). Roughly 10% of SigmaDO observations were positive indicating higher DO concentrations in bottom water than in surface, however, these SigmaDO values were all ≤ 0.6 mg/L. 25% of SigmaDO data occurred in the 0 and -1 mg/L range, and 25% of the data were ≤-4 mg/L indicating DO depletion with depth.

SigmaDO and SigmaSal appear to have a roughly linear relationship between 0 and 5 SigmaSal ‰ (Fig. 24). At SigmaSal ≥ 5 ‰, SigmaDO is mostly ≥ 3 mg/L, indicating DO depression at station 13385 is associated with salinity stratification. The relationship between SigmaSal and SigmaDO at station 13385 can be expressed by the line: SigmaDO = -1.3263 - 0.1822 * SigmaSal. Although $R^2 = 0.34$ is low, the coefficient values are highly significant, $P_a = 0.0025$, $P_b = 0.0002$.

STATION 13384

At station 13384, water column stratification appears to occur in late spring and summer (Fig. 25). In the example profiles plotted in Figure 25, bottom oxygen depletion was associated with water column stratification. In the case of August 1993, severe stratification (SigmaSal > 20 ‰) was associated with hypoxia. Depths of profile data for this station encompassed disparate depths. For example, depths of profiles taken November 2000 and July 1998 were < 2 m, whereas depths of profiles taken January 1990, May 1992, and August 1993 were > 10 m.

The distribution of SigmaSal values at station 13384 are skewed to the left (Fig. 26). Roughly 30% of SigmaSal observations were < 1 ‰. Approximately 20% of the observations were > 10 ‰, and 5.5% were > 20 ‰ indicating a highly stratified water body.

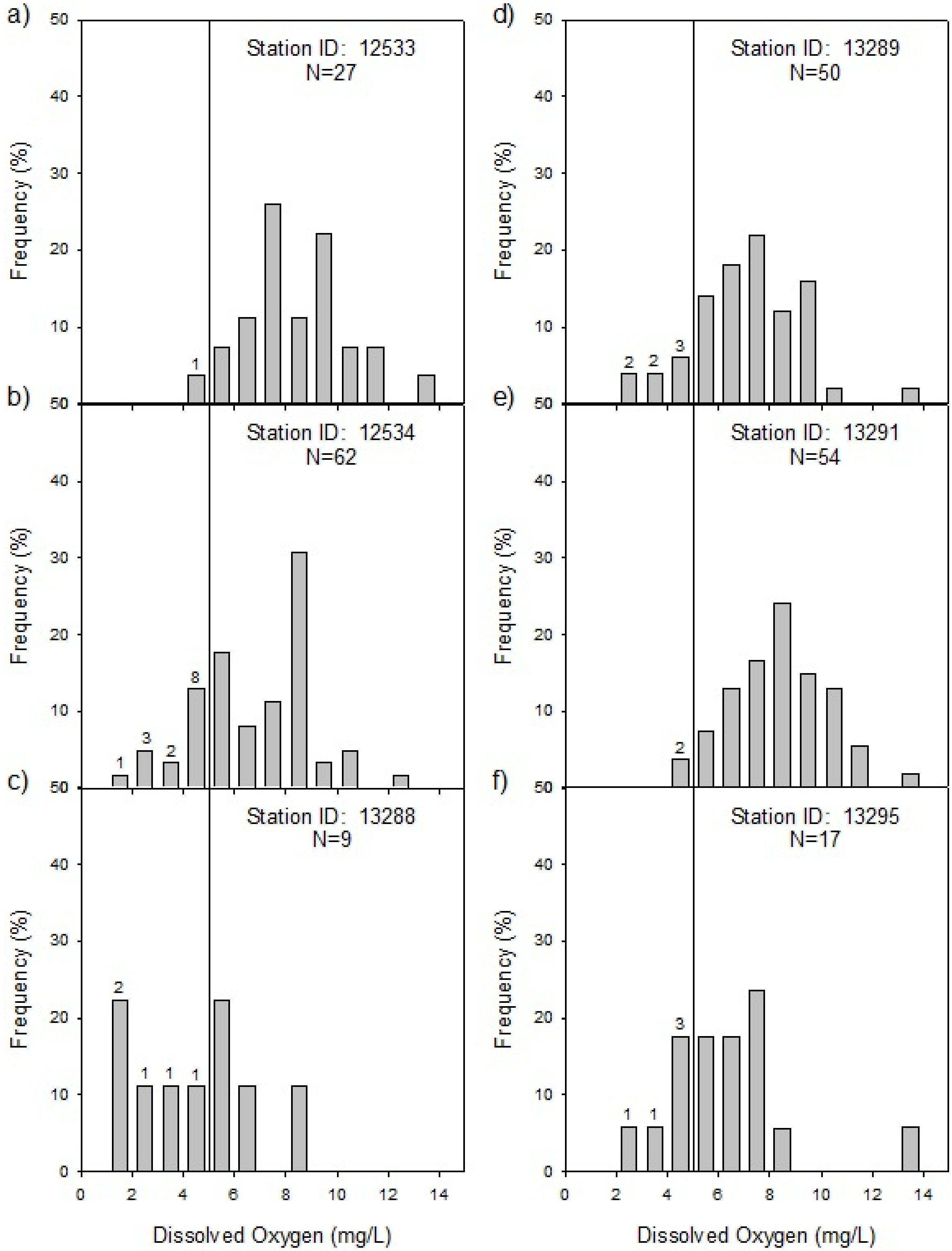


Figure 18: Frequency of observed dissolved oxygen values for TNRCC stations a) 12533, b) 12534, c) 13288, d) 13289, e) 13291, and f) 13295. X = 5 mg/L is the dissolved oxygen criteria. Numbers over bars are the number of observations within each category that is below the criteria.

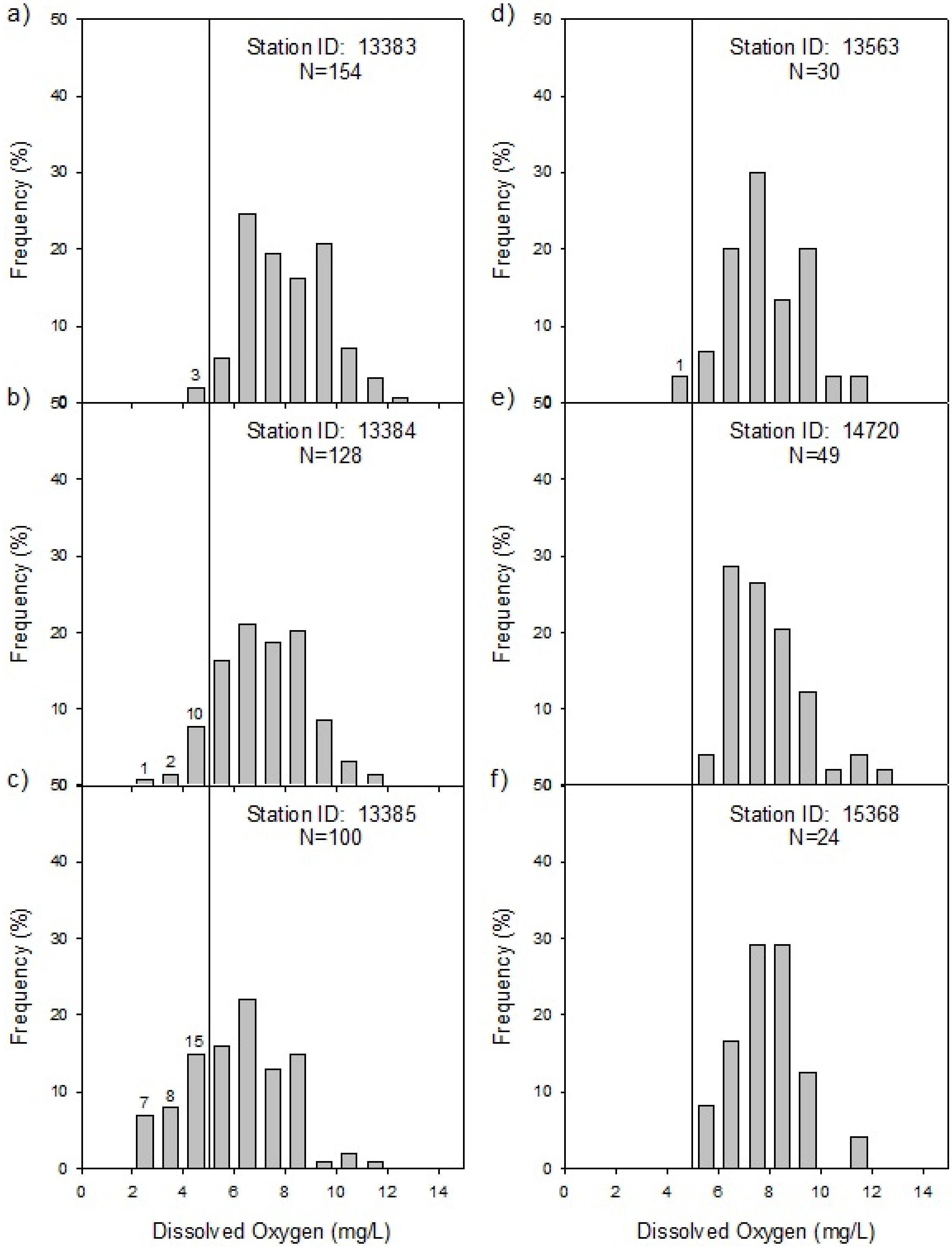


Figure 19: Frequency of observed dissolved oxygen values for TNRCC stations a) 13383, b) 13384, c) 13385, d) 13563, e) 14720, and f) 15368. X = 5 mg/L is the dissolved oxygen criteria. Numbers over bars are the number of observations within each category that is below the criteria.

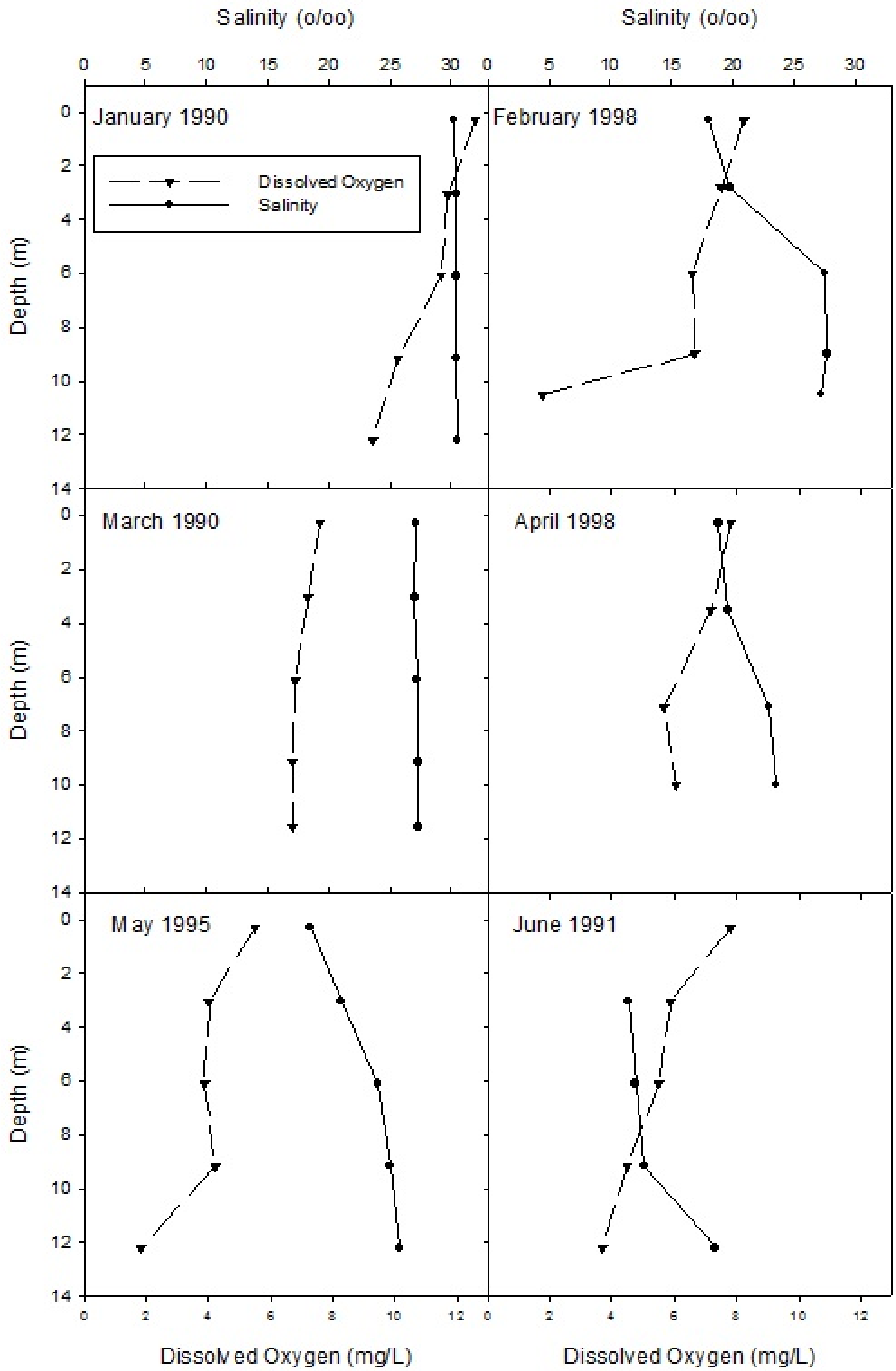


Figure 20: Station 13385, Alcoa Ship Dock. Example depth profiles of dissolved oxygen and salinity for months January - June.

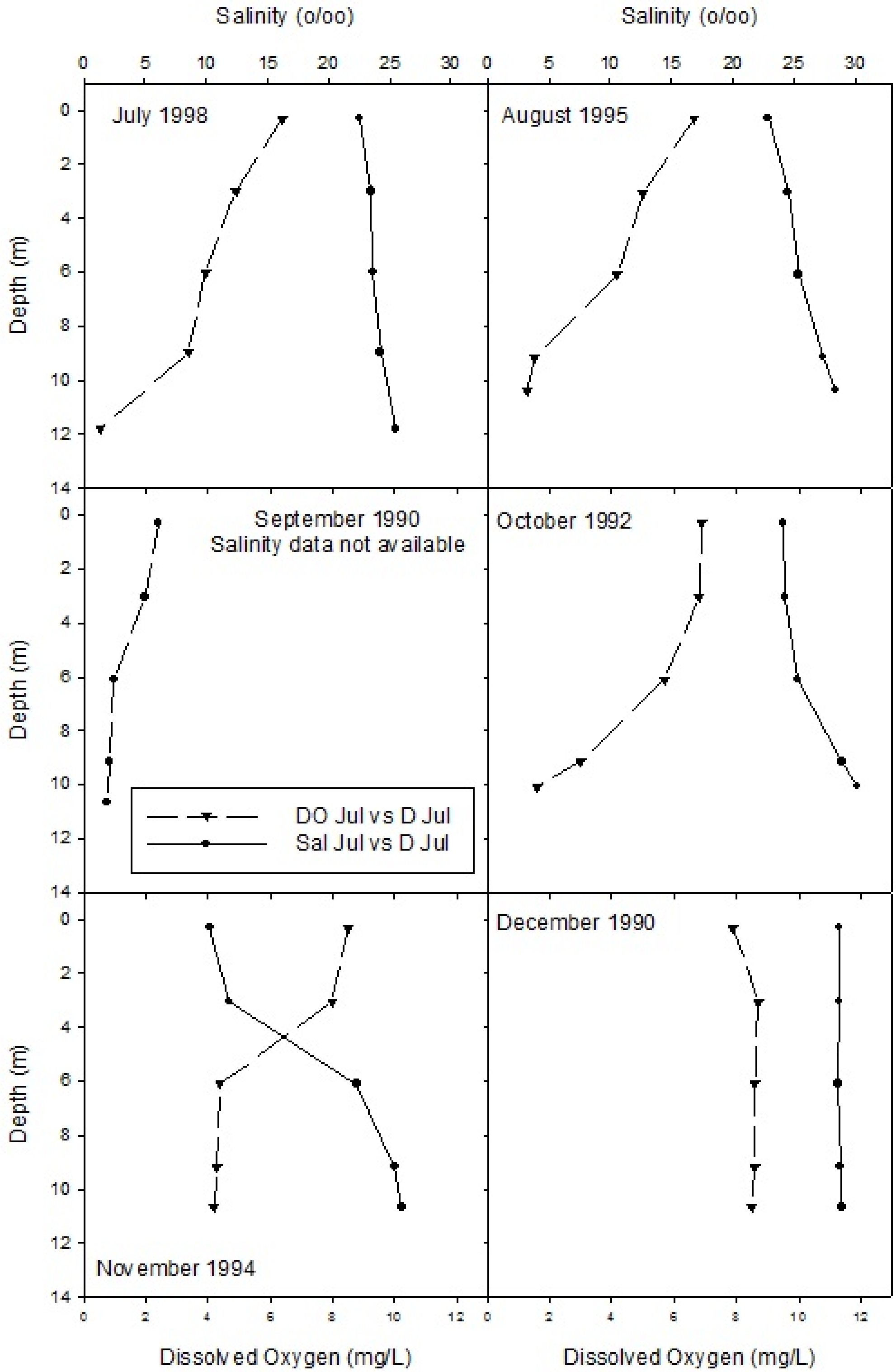


Figure 21: Station 13385, Alcoa Ship Dock. Example depth profiles of dissolved oxygen and salinity for months July - December.

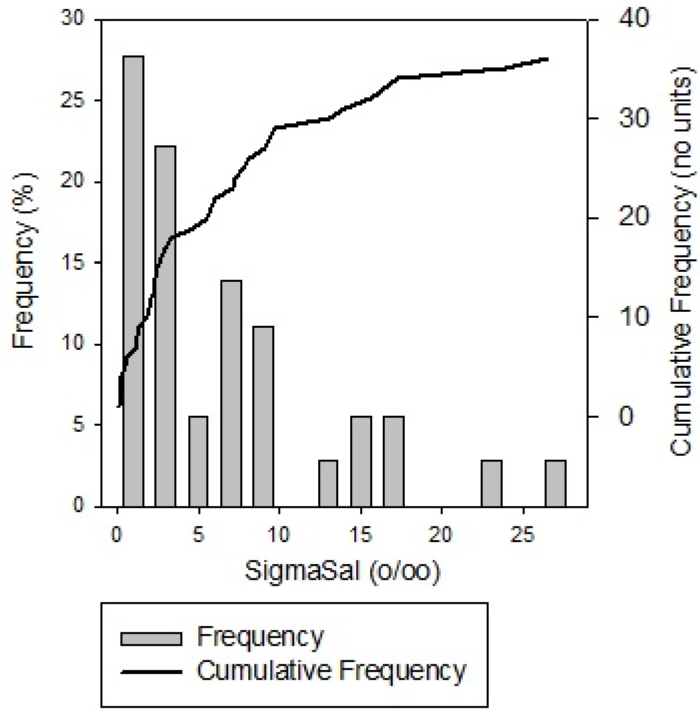


Figure 22: Frequency of SigmaSal values (o/oo) for Station 13385. N = 36, mean = 6.58, std. dev. = 6.79, min. = 0.1, and max. = 26.5.

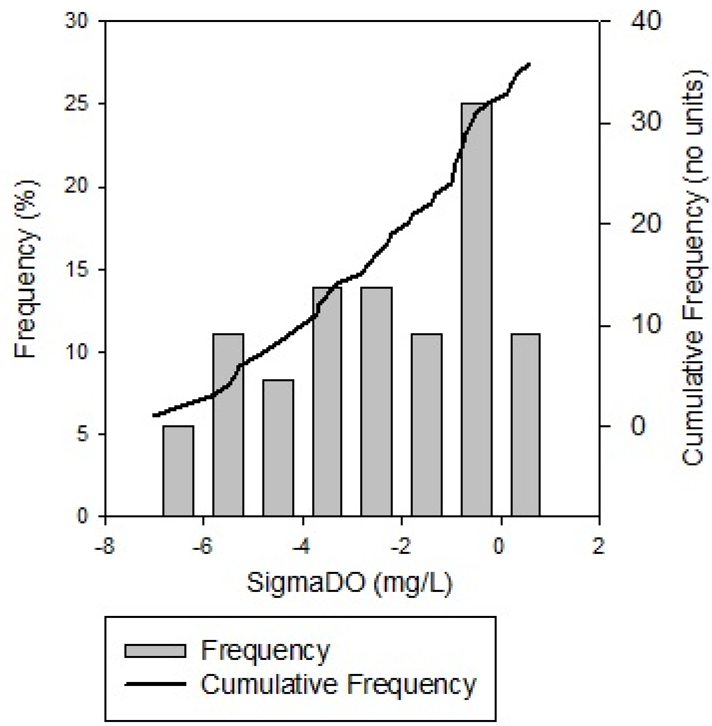


Figure 23: Frequency of SigmaDO values (mg/L) at Station 13385. N = 36, mean = -2.52, std. dev. = 2.11, min. = -7.00, and max. = 0.6.

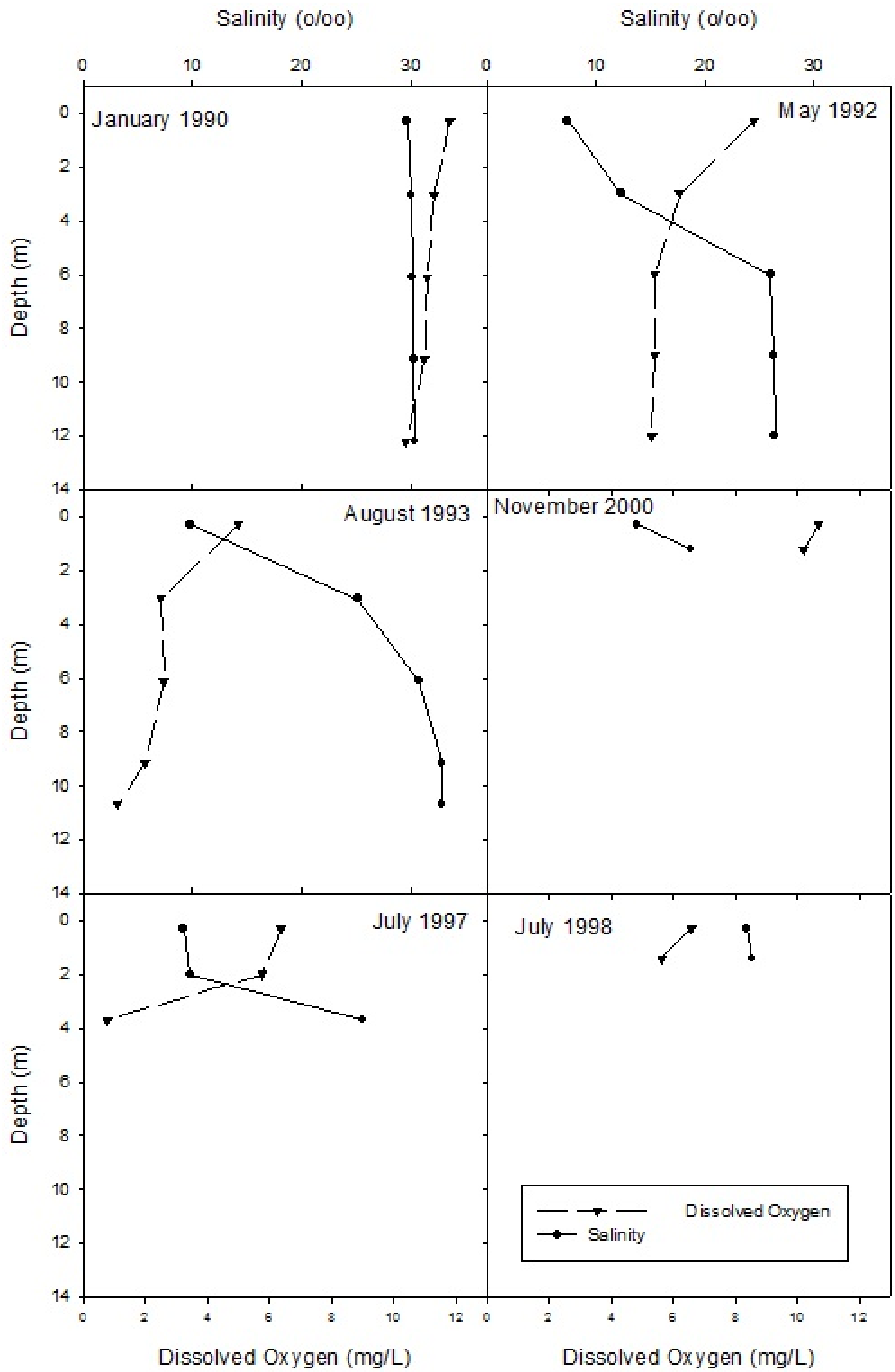


Figure 25: Station 13384, Y intersection of Port Lavaca and Matagorda Ship Channels at CM66. Example depth profiles of dissolved oxygen and salinity.

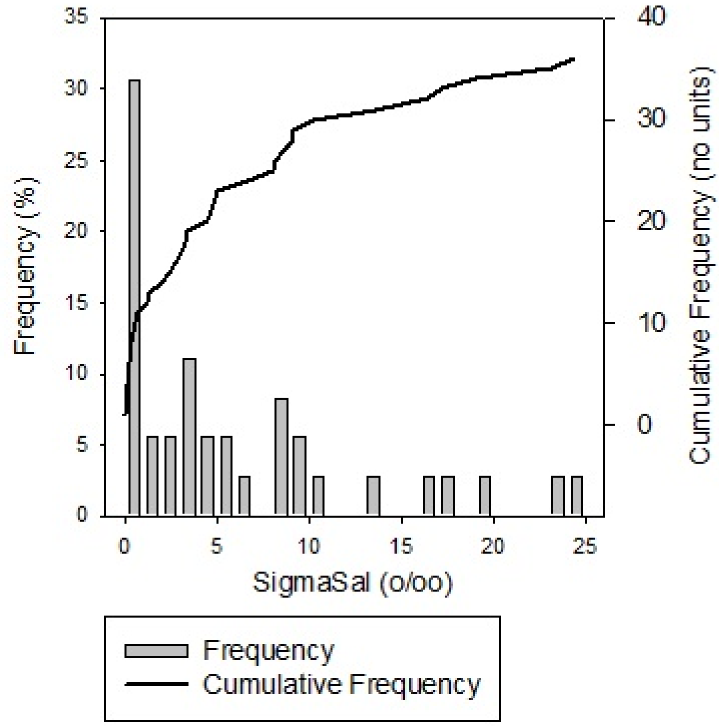


Figure 26: Frequency of SigmaSal values (o/oo) for Station 13384. N = 36, mean = 6.01, std. dev. = 6.79, min. = 0, and max. = 24.4.

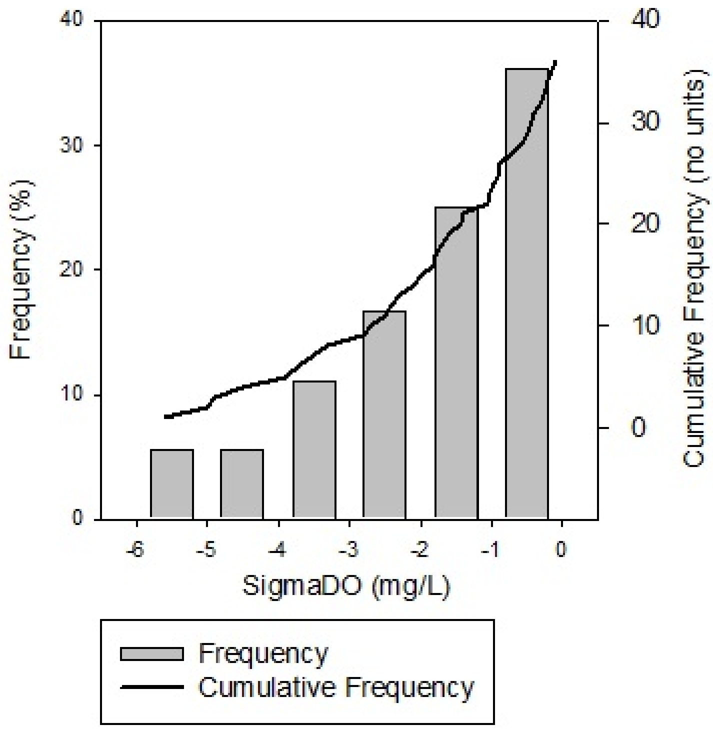


Figure 27: Frequency of SigmaDO values (mg/L) at Station 13384. N = 36, mean = -1.92, std. dev. = 1.53, min. = --5.59, and max. = -0.1.

The distribution of SigmaDO observations were skewed to the right (Fig. 27). More than 60% of the observations were > -2 mg/L. No positive values were found. Eleven percent of the observations were < -4 mg/L.

The relationship between SigmaSal and SigmaDO appears to be negative and linear (Fig. 28). As SigmaSal becomes large, the spread in SigmaDO increases such that SigmaSal of ~15 ‰ could have a SigmaDO ranging from -2 to -5 mg/L. The relationship between SigmaSal and SigmaDO at station 13384 can be expressed by the line: SigmaDO = -0.9240 - 0.1658 * SigmaSal. For this equation, R^2 = 0.54 and the coefficient values are highly significant, P_a = 0.0004, and P_b < 0.0001.

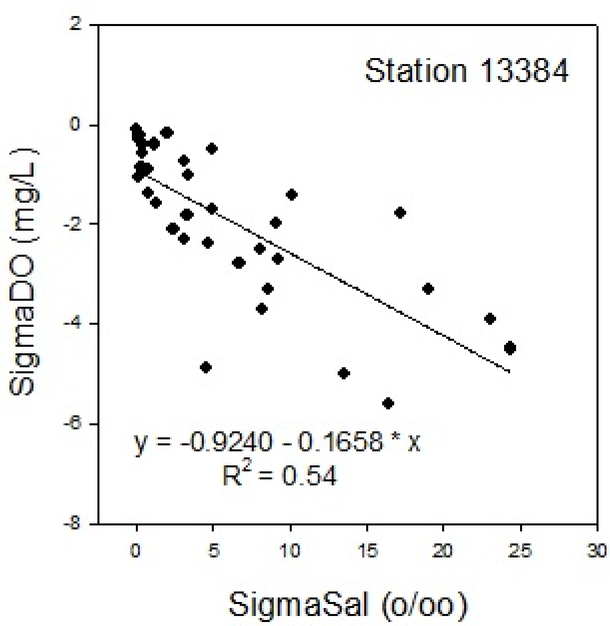


Figure 28: Plot of SigmaSal and SigmaDO at Station 13384.

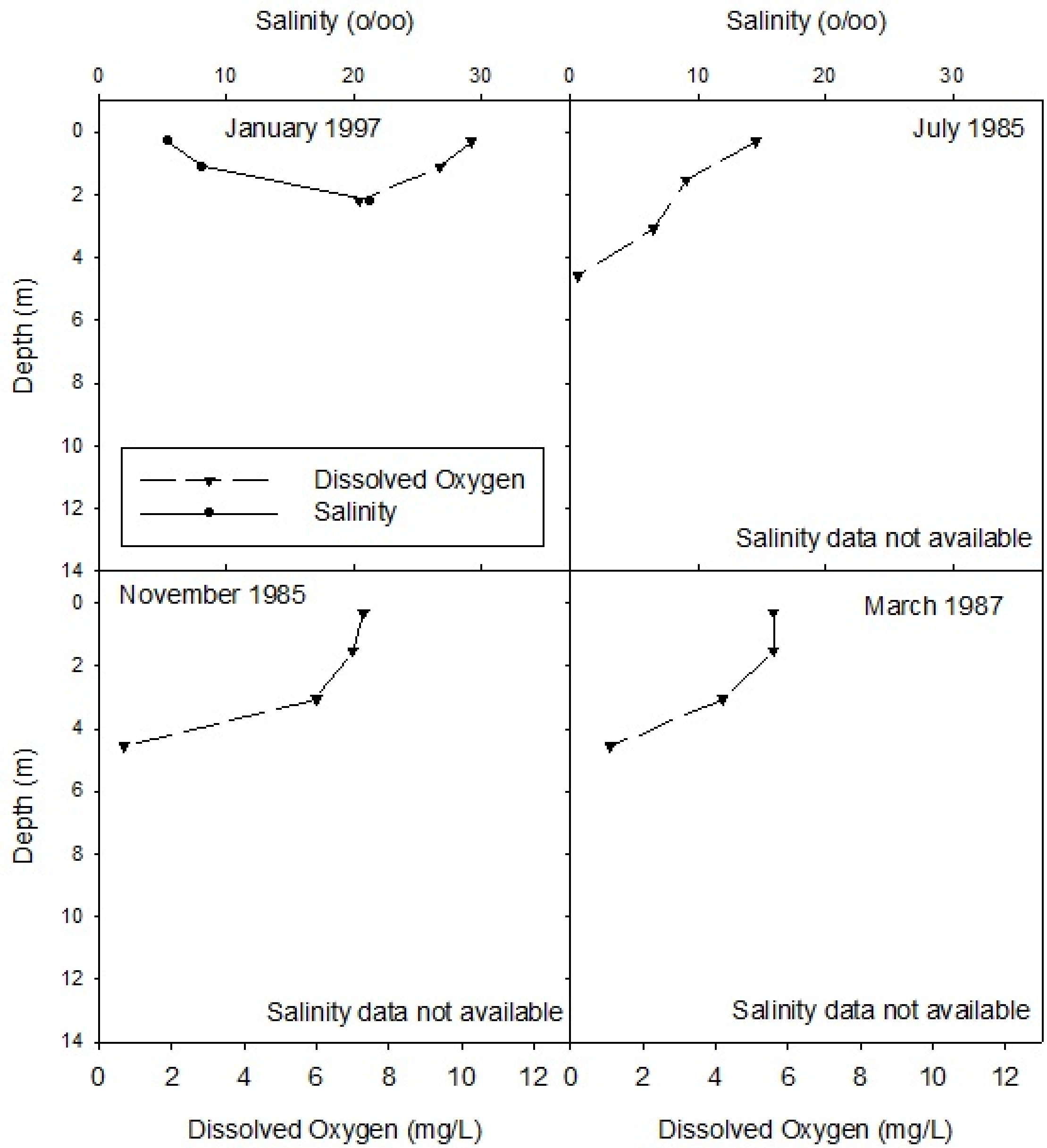


Figure 29: Station 12534, Lynn's Bayou. Example depth profiles of dissolved oxygen and salinity.

STATION 12534

Depth profiles for salinity were only available for one sampling, January 1997 (Fig. 29). In 7 of the 10 DO profiles, oxygen depletion with depth was apparent. In 3 DO profiles, bottom hypoxia was recorded (Fig. 29). Hypoxia does not appear to be season specific. Because of the sparsity of salinity and dissolved oxygen data for this station, SigmaSal and SigmaDO were not calculated.

At station 13383, water column stratification and bottom oxygen depletion can occur during any season (Fig. 30). No bottom hypoxia was found.

The distribution of SigmaSal observations was skewed to the left with 45% of the values being < 1 ‰ (Fig. 31). Roughly 21% of the values were > 4 ‰.

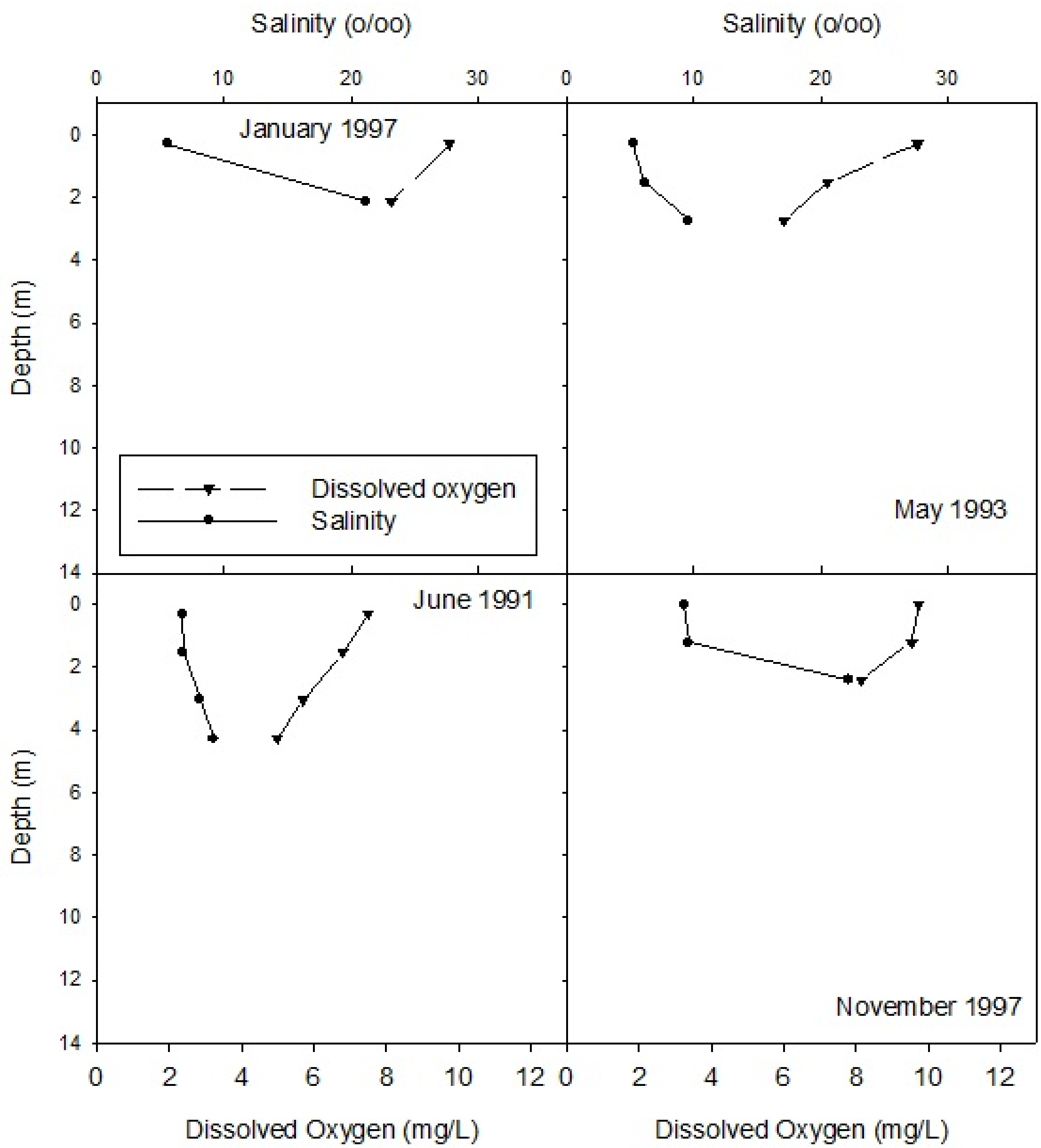


Figure 30: Station 13383, Lavaca Bay at SH35 Causeway. Example depth profiles of dissolved oxygen and salinity.

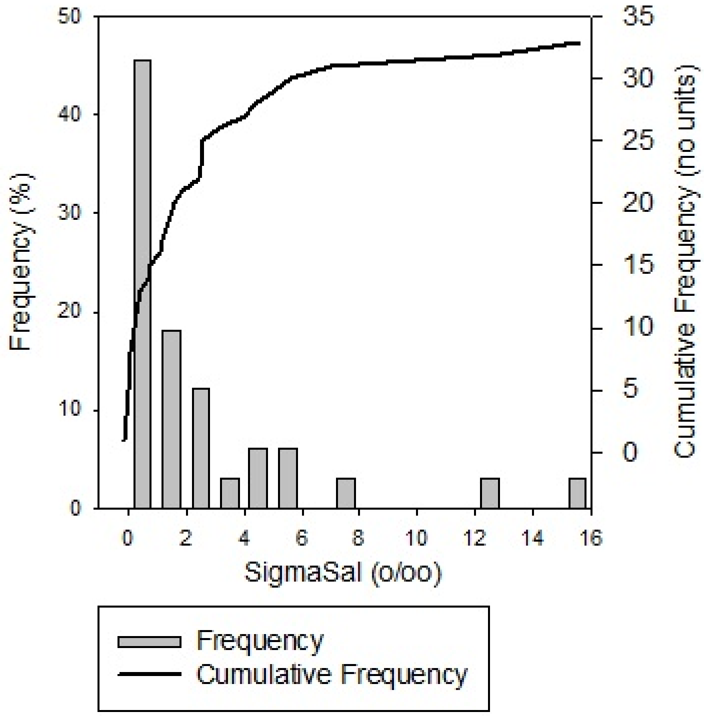


Figure 31: Frequency of SigmaSal values (o/oo) for Station 13383. N = 33, mean = 2.42, std. dev. = 3.57, min. = -0.1, and max. = 15.6.

The distribution of SigmaDO observations was skewed slightly to the right (Fig. 32). A clear majority, 75%, of SigmaDO observations at station 13383 were > -1 mg/L, with 12% being between 0 and 1 mg/L. No observation < -4 mg/L were found.

The relationship between SigmaSal and SigmaDO for station 13383 shows a general decrease of Sigma DO with an increase of SigmaSal, and is in the form of a shotgun pattern (Fig. 33). The relationship between SigmaSal and SigmaDO at station 13385 can be expressed by the line: SigmaDO = -0.6230 - 0.1048 * SigmaSal. Although $R^2 = 0.17$ is low, the coefficient values are significant, $P_a = 0.0016$, and $P_b = 0.0187$.

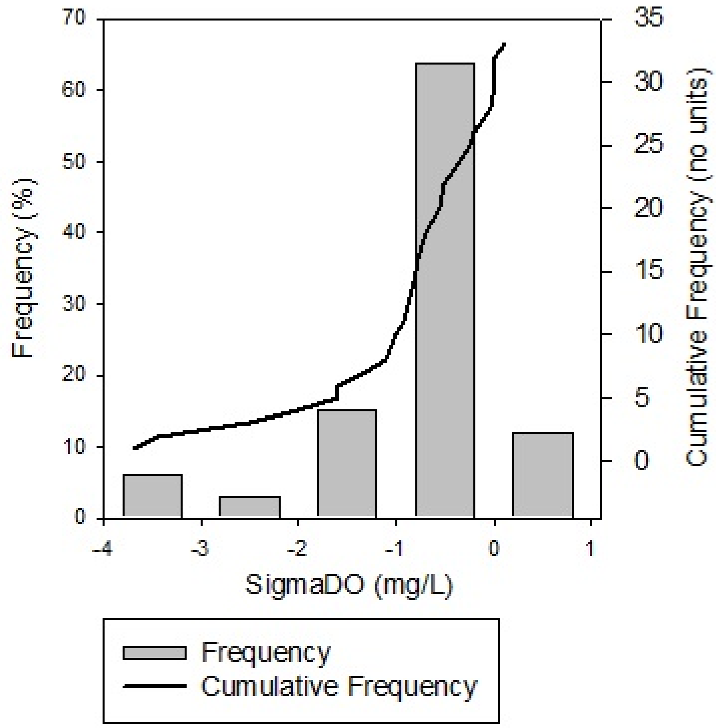


Figure 32: Frequency of SigmaDO values (mg/L) at Station 13383. N = 33, mean = -0.88 std. dev. = 0.92, min. = --3.7, and max. = -0.1.

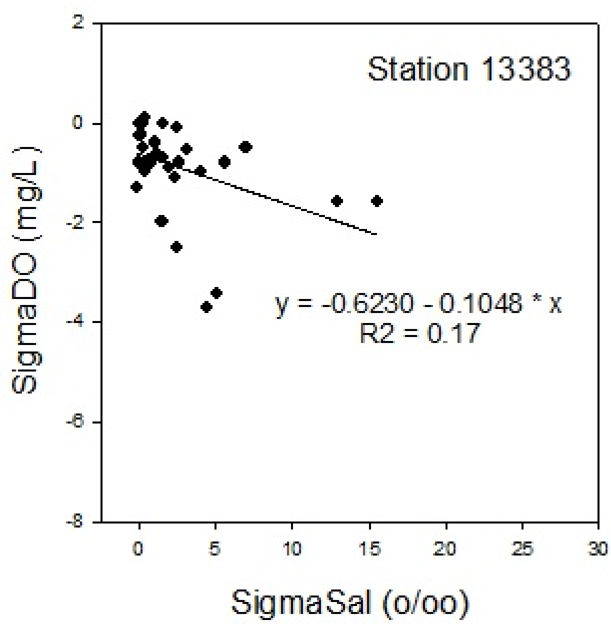


Figure 33: Plot of SigmaSal and SigmaDO at Station 13383.

STATION 13563

Station 13563 is shallow (Fig. 34) with a maximum measured depth of 4.5 ft. Only slight stratification and oxygen depletion was found at station 13563 (Fig. 34). No instances of hypoxia were recorded.

The distribution of SigmaSal observations was skewed to the left with more than 80% of the values being < 1 ‰ (Fig. 35). One observation (~4%) was > 3 ‰.

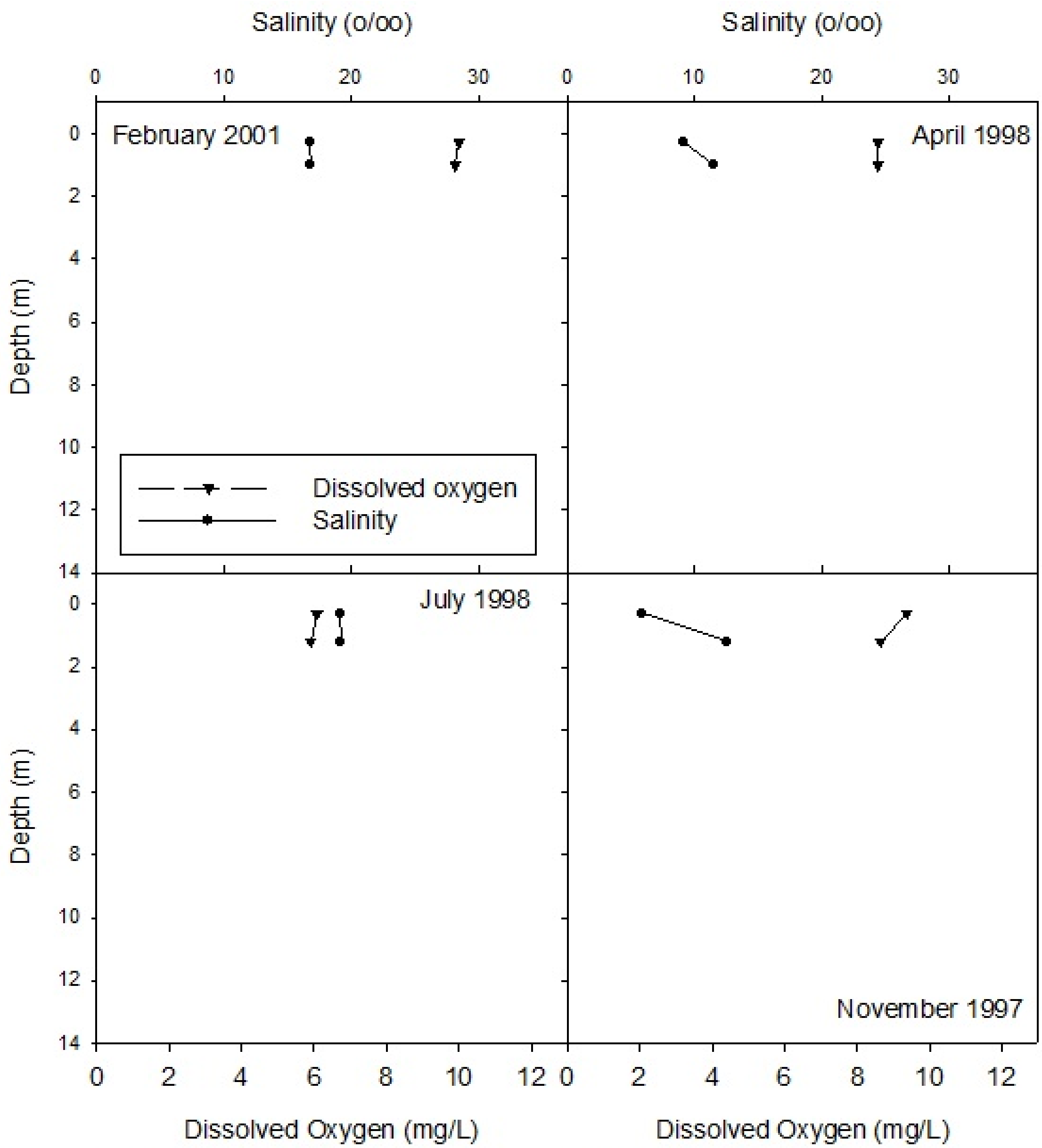


Figure 34: Station 13563, Lavaca Bay at CM 22 in Red Bluff Channel. Example depth profiles of dissolved oxygen and salinity.

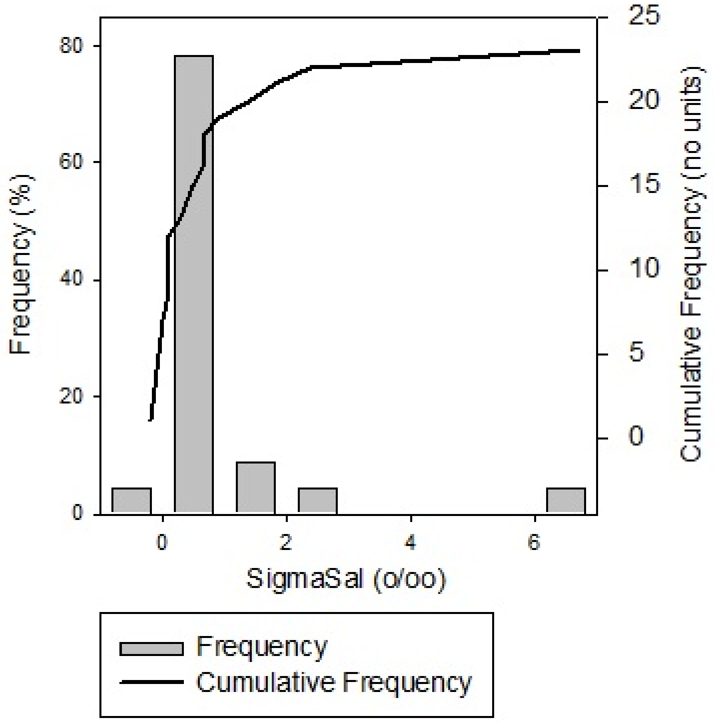


Figure 35: Frequency of SigmaSal values (o/oo) for Station 13563. N = 23, mean = 0.73, std. dev. = 1.45, min. = -0.2, and max. = 6.7.

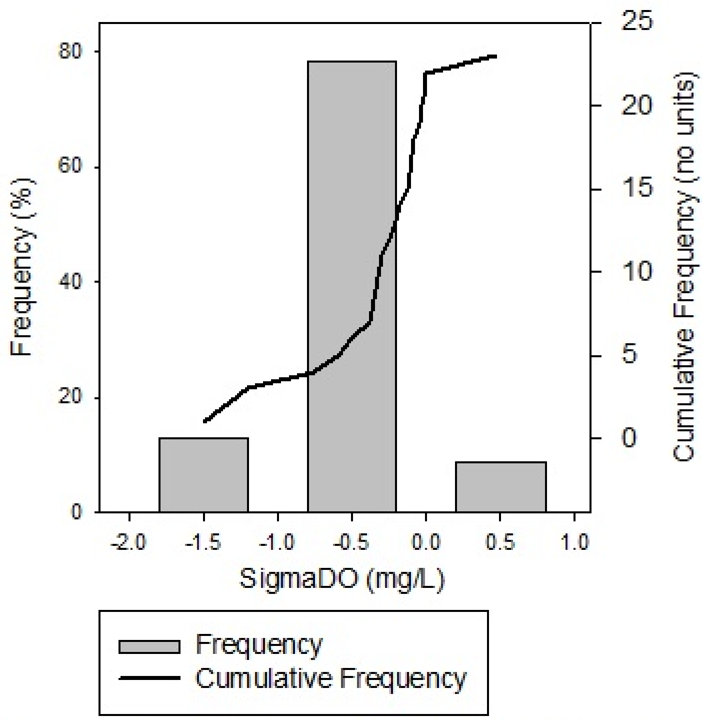
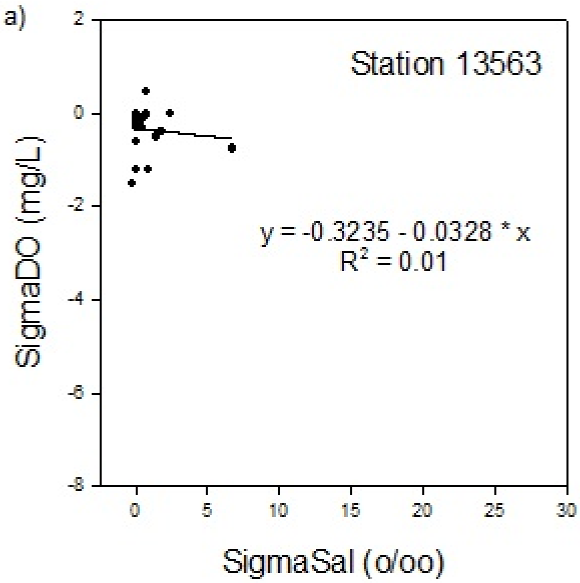


Figure 36: Frequency of SigmaDO values (mg/L) at Station 13563. N = 23, mean = -0.35 std. dev. = 0.45 min. = -1.5, and max. = 0.47.

The distribution of SigmaDO observations was narrow ranging from -2 to 1 mg/L (Fig. 36). The majority (87%) of the data was > -1 mg/L. No observations were found < -4 mg/L.

The ranges of SigmaSal and SigmaDO were narrow; SigmaSal ranged between -0.2 and 6.7 ‰ and SigmaDO ranged between -0.01 and -1.5 mg/L. There does not appear to be a clear relationship between SigmaSal and SigmaDO (Fig. 37). The lack of a relationship was confirmed by linear regression. Linear regression resulted in the line: SigmaDO = -0.3235 - 0.0328 * SigmaSal. For this equation, R^2 = 0.01 and only one of the coefficient values is significant, P_a = 0.0065, and P_b = 0.6298. A second regression was conducted after omitting the outlier at SigmaSal = 6.7 ‰ and SigmaDO = -0.76. The regression conducted without the outlier resulted in the line: y = -0.3808 + 0.1146 * x. For this equation, R^2 = 0.03 and only one of the coefficient values is significant, P_a = 0.0044, and P_b = 0.4551.

a)



b)

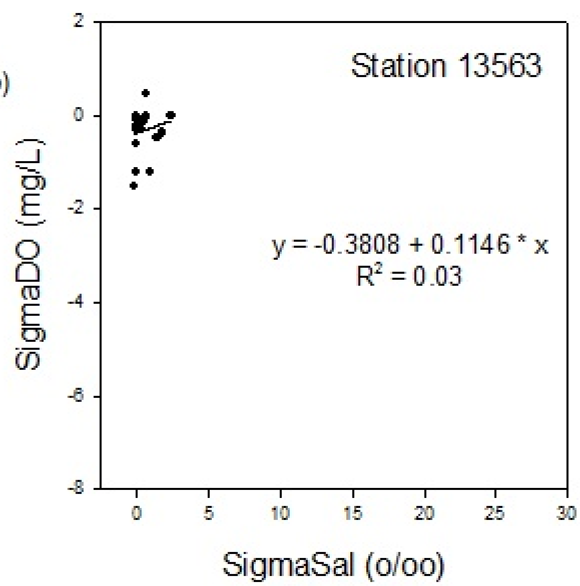


Figure 37: Plot of SigmaSal and SigmaDO at Station 13563. a) includes all SigmaDO and SigmaSal data for station 13563. b) the outlier is omitted for linear regression.

Table 5: TNRCC 24-hr DO data. The criteria for 24-hr average and 24-hr minimum DO are 5 mg/L and 4 mg/L respectively. Values lower than these are considered exceedences and are 14-pt bolded.

Date	**TNRCC Stations**					
	13385		**13383**		**13384**	
	24-hr average	24-hr minimum	24-hr average	24-hr minimum	24-hr average	24-hr minimum
03 May 2002	5.92	5.37				
24August 2001			5.00	**3.46**		
08 August 2001	5.73	4.97	5.14	4.52	6.05	5.10
03 May 2001	6.44	5.91			6.79	6.49
28 June 2000	5.90	4.30	6.80	5.00	6.00	4.60

24-hr DO

A total of 10 24-hr DO observations were available from the TNRCC (Table 5). Of these observations, only one exceeded the TNRCC criteria of high aquatic life use. On August 24, 2001, the observed 24-hr DO minimum was 3.46 mg/L, lower than the DO minimum criteria of 4 mg/L.

Review of Texas Parks and Wildlife Data

The Texas Parks and Wildlife Department's (TPWD) Lavaca Bay grab-sample data covered the period September 1975 - December 1999 and included 3576 grab-sample observations. Dissolved oxygen data was available for 3074 of these observations. Only two observations were hypoxic (i.e., DO < 2 mg/L). One hypoxic observation was not stationed in Lavaca Bay, but above it, as part of the TPWD's Lake Texana hydrographic survey conducted in 1984. The other hypoxic observation occurred in 1992 and was located at 28 40'20"N -96 38' 20"W in the western part of upper Lavaca Bay, south of Garcitas Cove. Only 118, roughly 4% of total DO observations, were < 5 mg/L DO and 0.8% were < 4 mg/L DO.

Of the 3576 hydrographic observations available, 975 were taken at the surface (depth = 0.3 m) with 962 observations including DO. The total range of DO values was 0.7 - 16.7 mg/L. Approximately 84% of DO values were in the range 5.4 - 10.2 mg/L (Fig. 38). Only one observation (0.1% of DO observations) was hypoxic; it was mentioned previously. Only 33 DO observations, roughly 3.4% of total DO observations, were < 5 mg/L DO and 5, or 0.5%, were < 4 mg/L DO.

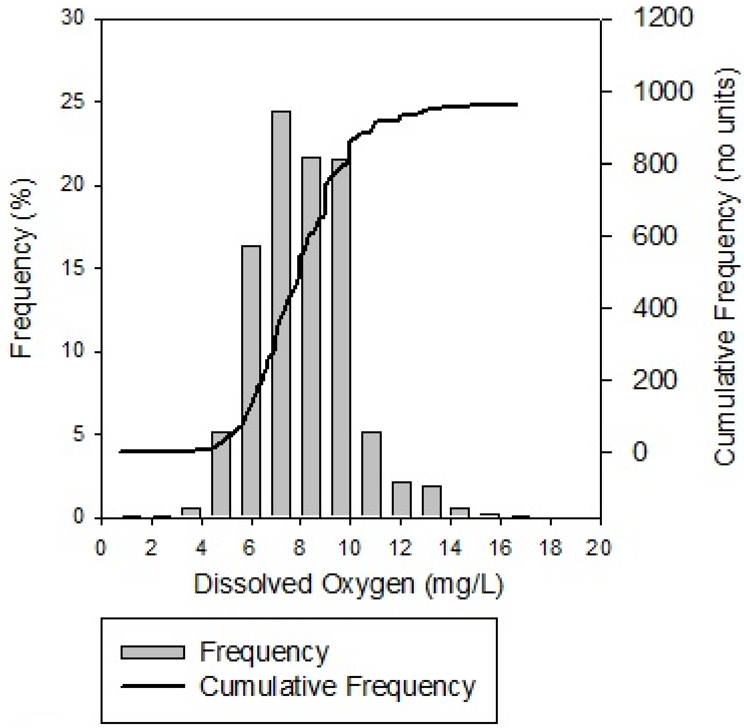


Figure 38: Frequency of dissolved oxgyen values (mg/L) from the Texas Parks and Wildlife Department. N = 962, mean = 8.01, std. dev. = 1.93, min. = 0.7, and max. = 16.7.

Surface salinity observations ranged 0 - 37 ‰ (Fig. 39). The frequency distribution of salinity values is irregular, but demonstrates that Lavaca Bay is as frequently fresh as it is saline up to 31.5‰ . Roughly 2.3% of salinity observations were > 31.5‰. The average salinity in Lavaca Bay is 15.91 ‰.

Surface temperature observations ranged between 2.1 and 35 °C (Fig. 40). Approximately 80% of these observations were in the range 16 - 32 °C. The mean temperature was 23.25 °C.

Plots of TPWD surface data by Julian date demonstrate trends for temperature and DO, but not for salinity nor turbidity (Fig. 41). Figure 41a demonstrates expected annual warming of water temperature during the summer. Figure 41d demonstrates a annual decline in DO concomitant with the annual warming.

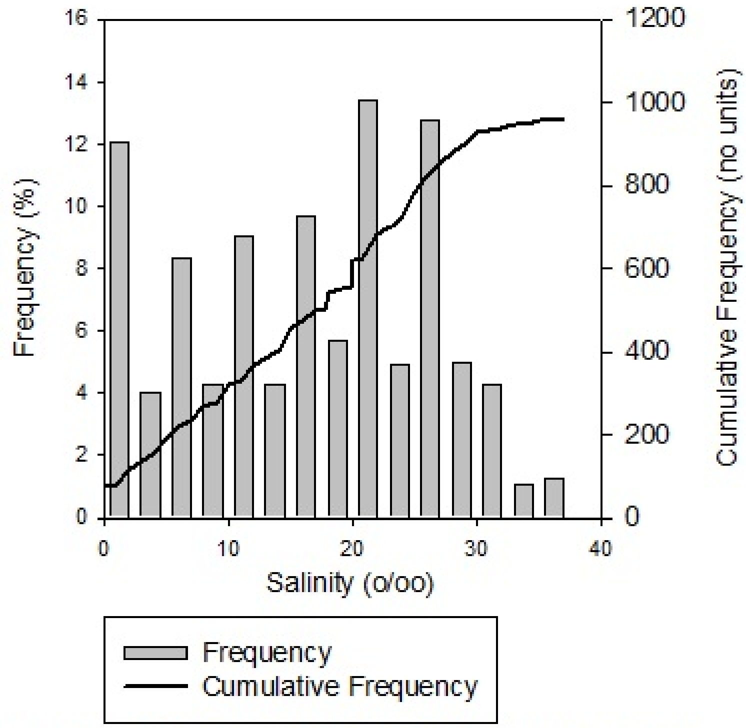


Figure 39: Frequency of salinity values (o/oo) from the Texas Parks and Wildlife Department. N = 962, mean = 15.91, std. dev. = 9.60, min. = 0.00, and max. = 37.00.

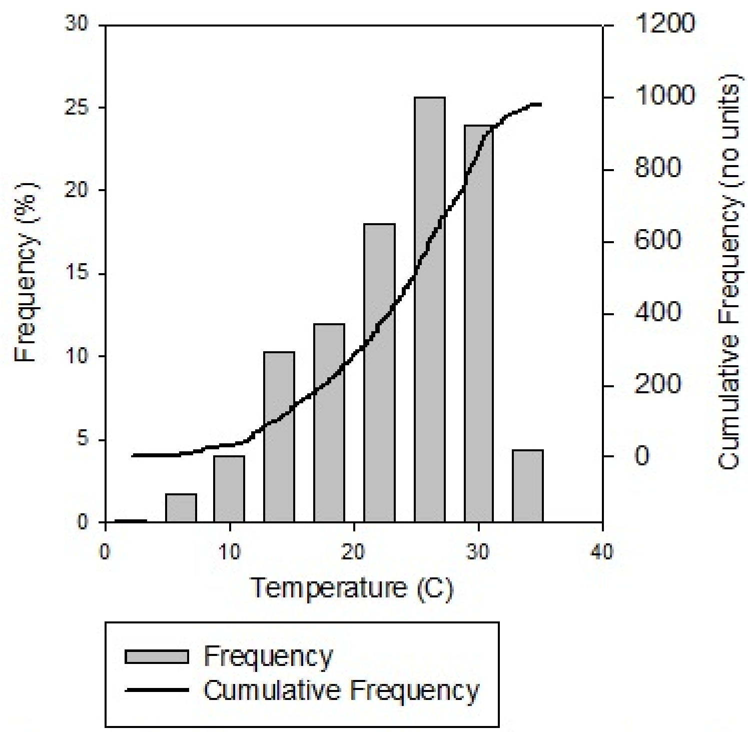


Figure 40: Frequency of temperature values (C) from the Texas Parks and Wildlife Department. N = 975, mean = 23.25, std. dev. = 6.51, min. = 2.10, and max. = 35.

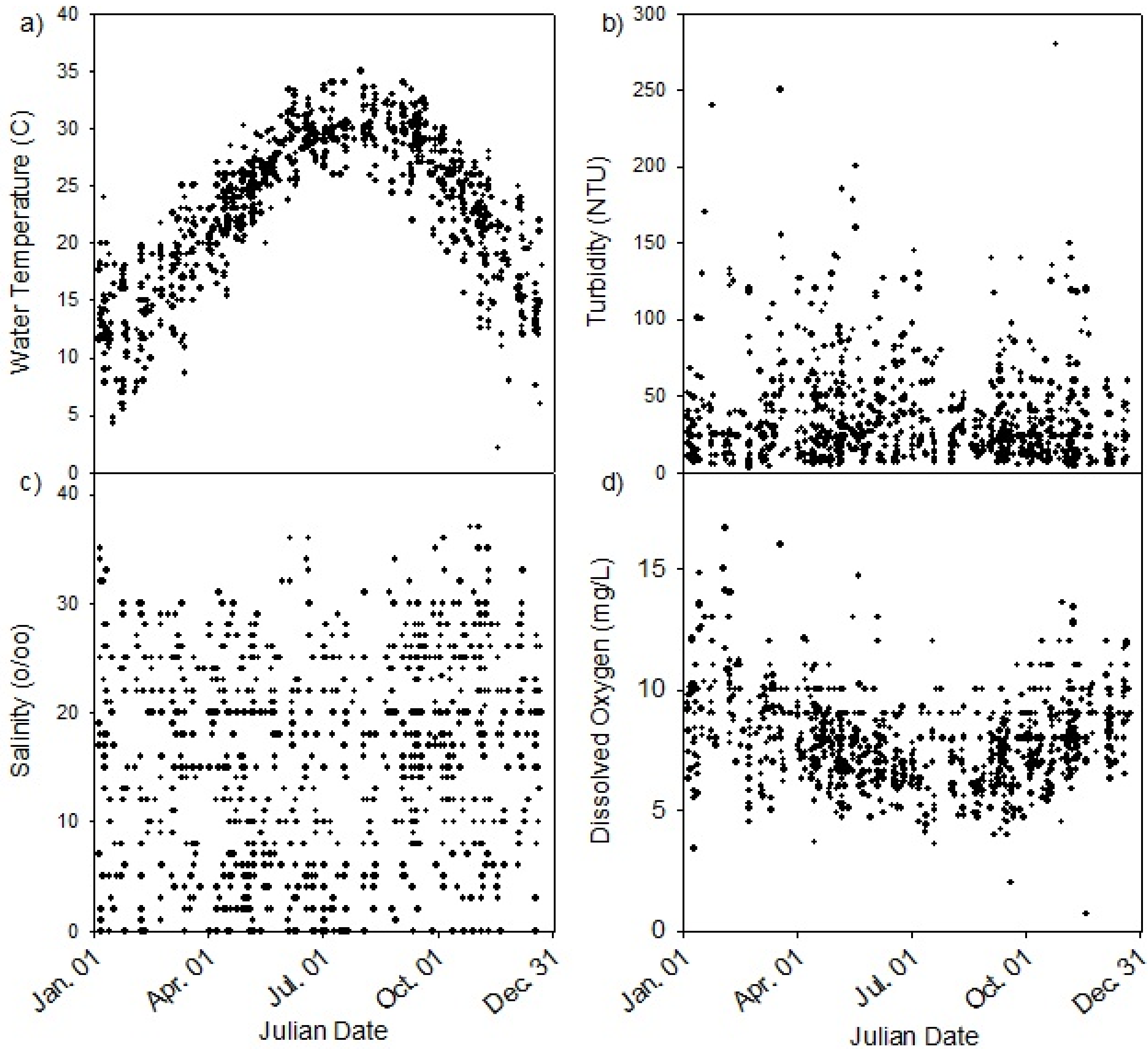


Figure 41: Texas Parks and Wildife Department parameter values plotted by the julian day of the year. a) Water temperature, b) turbidity, 3) salinity, and d) dissolved oxygen.

Review of Formosa Plastics, Corp, Texas Data

Sixteen stations were represented in the Formosa data set. Hydrographic data obtained from Formosa Plastics, Corp, Texas (Formosa) covered the period May 1993 - January 2002. A total of 19 stations were represented in the dataset. Fifteen of these stations radiated out from around the diffuser (near TNRCC station 13563), the remaining 4 stations were scattered in upper Lavaca Bay (north of Hwy 35).

Nutrient data was obtained from Formosa for the period July 1998 - April 2001. Nutrient parameters included in this dataset are: ammonia nitrogen, nitrite nitrogen, nitrate nitrogen, total phosphorous, and ortho-phosphorous. When data for these parameters are plotted across the Julian year, no annual trends are discernable (Fig.42).

The Formosa dataset also included a total of 674 grab-sample observations. The variables collected are conductivity, salinity, temperature, pH, and DO; not all variables were collected for each observation. No incidences of hypoxia were observed in Formosa's dataset. Four DO observations (0.6%) were < 5 mg/L DO, but none of these were < 4 mg/L DO.

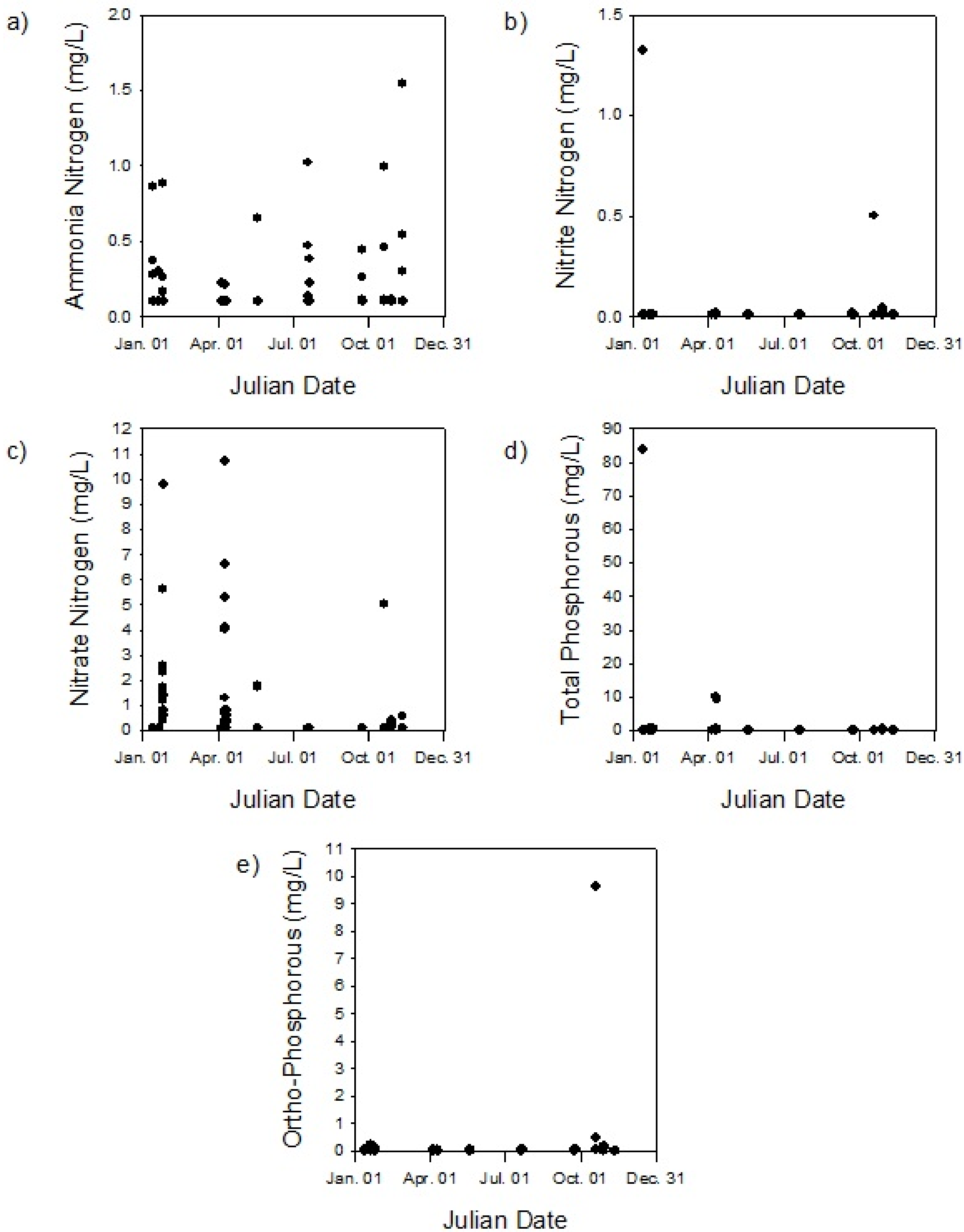


Figure 42: Formosa Plastics' nutrient data plotted accross the Julian year for: a) ammonia nitrogen, b) nitrite nitrogen, c) nitrate nitrogen, d) total phosphorous, and e) ortho-phosphorous.

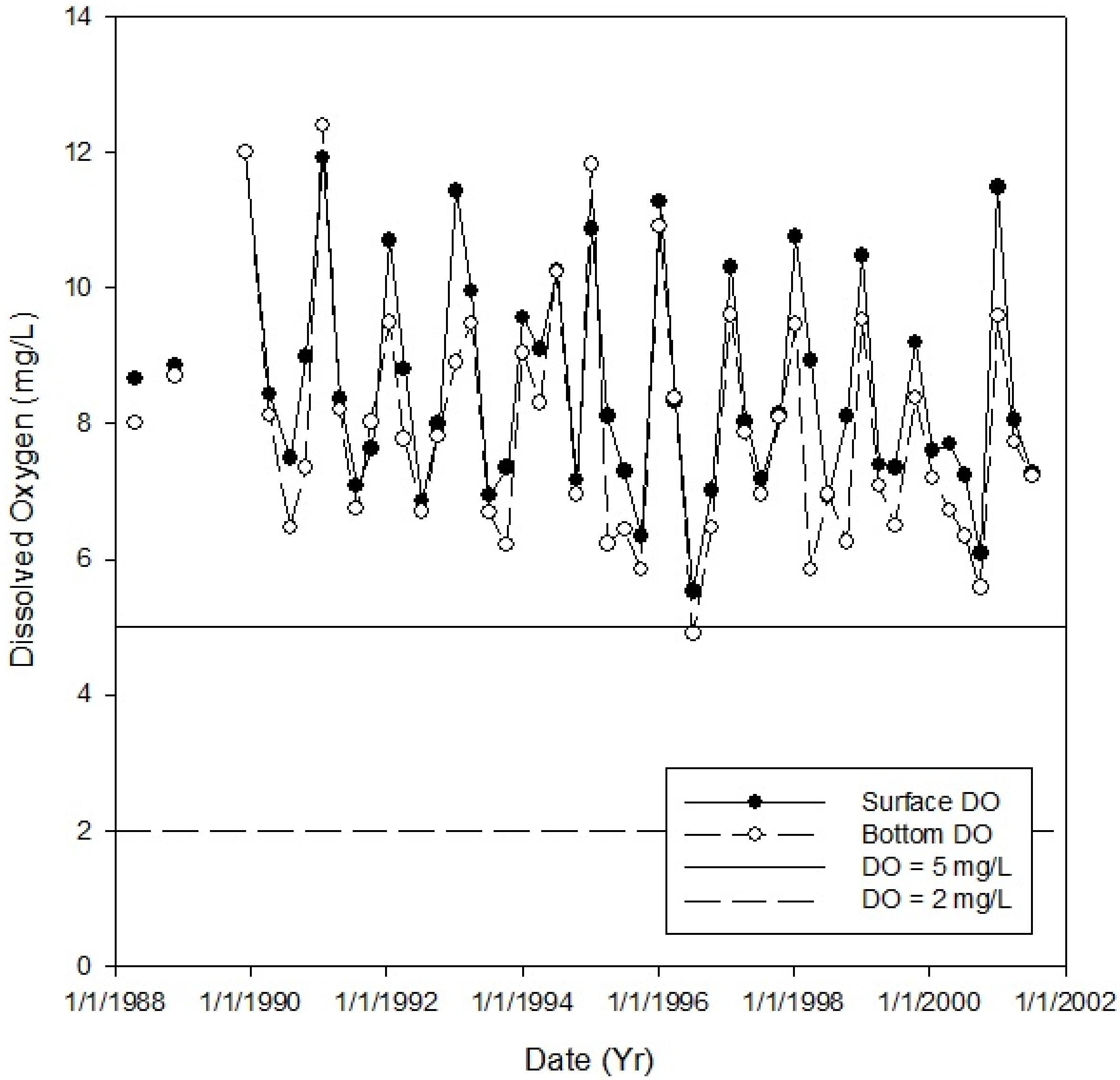


Figure 43: Historical dissolved oxygen data taken by the University of Texas Marine Science Institute.

Review of UTMSI Data

Discrete, grab-sample DO data was available from UTMSI for the period April 1988 - July 2001 for two stations in Lavaca Bay. Of a total of 240 hydrographic observations that were recorded during this period, 195 contained DO data. Only one DO observation was less than 5 mg/L (Fig.43). It was taken on July 9, 1996 at station B (TNRCC station 17554), at a depth of 1.6 m.

Sediment TOC was measured for stations A and B (TNRCC stations 17553 and 17554 respectively) on three dates: 14 October 1996, 17 October 1997, and 21 October 1999. At station A, sediment TOC ranged between 0.34 and 1.37 in the 0 - 1 cm section, and 0.66 - 0.78 in the 2 - 3 cm section. At station B, sediment TOC ranged between 0.71 - 1.00 in the 0 - 1 cm section, and 0.75 - 0.84 in the 2 - 3 cm section.

Surface (0 - 3 cm) sediment N was measured as part of CHN analysis for stations A and B on three dates: 14 October 1996, 17 October 1997, and 21 October 1999. Sediment N in deeper sediment layers is also available for these and other dates. At station A, sediment N ranged 0.075 - 0.110 in the 0 - 1 cm section, and 0.070 - 0.084 in the 2 - 3 cm section. At station B, sediment N ranged 0.077 - 0.115 in the 0 - 1 cm section, and 0.073 - 0.087 in the 2 - 3 cm section.

Review of Alcoa Data

Alcoa collected hydrographic and TOC data from ten stations during the period 02 July 1996 - 04 December 1996. All of these stations were within the Superfund Site and most were within the region closed by the Texas Department of Health. Hydrographic data collected were: salinity, temperature, DO, and Redox potential (Eh). All DO measurements were > 6 mg/L. Filtered TOC measurements ranged between 1.86 - 2.81 mg/L. Unfiltered TOC measurements ranged between 1.95 - 9.23 mg/L.

Review of TWDB Data

24-hr DO data was available on the internet from the TWDB for the period December 1986 - March 21 2002 at the time of dat base query. The TWDB makes no warranties concerning this data stating on the website: "These data are raw, uncorrected, and may contain errors. The Board makes no warranties (including no warranties as to merchantability or fitness) either expressed or implied with respect to the data or its fitness for any specific application." However, the TWDB is presently putting together a quality assurance (QA) document that documents their methodology and QA procedures.

TWDB data was collected at only one station that is very nearly the same location as where TNRCC's station 13383 is sampled. The sonde was placed at mid-water which, assuming a well-mixed estuary, is ½ the depth of the mixed surface layer. The actual depth of deployment varied through the period evaluated, ranging from 2.32 to 6.98 ft from the water surface. The typical depth of sonde deployment was between 4 and 5 ft.

Only data dating back to September of 1997 was evaluated (Table 6). A total of 41 24-hr observations were available for the period spanning September 1997 to the present (Fig. 44). Of these, 8 observations (20%) exceeded the TNRCC criteria for 24-hr DO average (5 mg/L), and 14 observations (34%) exceeded the TNRCC criteria for 24-hr DO minimum (4 mg/L; Figs. 44 and 45). Only 2 observations were hypoxic. Seventy-five percent of 24-hr minimum DO

Table 6: Texas Water Development Board 24-hr DO data. Sonde deployed near TNRCC station 13383. The criteria for 24-hr average and 24-minimum DO are 5 mg/L and 4 mg/L, respectively. Values lower than these are exceedences. Exceedences of TNRCC criteria are in bold typeface.

Begin Date	***Min. DO***	***Avg. DO***	***Max DO***	***n***
3/21/02	7.41	8.34	8.87	24
2/18/02	6.4	7.32	8.26	24
1/21/02	7.02	7.9	8.5	24
10/26/01	5.25	5.94	7.82	24
9/19/01	4.9	5.68	7.18	24
8/15/01	4.6	6.1	7.72	24
7/20/01	5.03	5.91	6.63	24
6/28/01	***2.4***	***4.18***	5.07	24
6/6/01	5.57	6.87	7.98	24
4/19/01	5.38	6.29	7.18	24
3/29/01	5.94	7.29	8.15	24
9/29/00	9.72	10.44	10.94	24
8/23/00	***2.88***	***4.71***	6.22	24
7/24/00	***3.26***	***4.58***	5.93	24
5/30/00	4.26	5.33	6.52	24
4/13/00	5.46	6.82	7.55	24
3/10/00	6.68	7.08	7.55	24
1/5/00	5.62	7.39	8.47	24
10/25/99	5.89	7.48	8.31	24
9/22/99	***3.13***	***4.62***	5.71	24
8/18/99	***2.75***	***4.47***	6.07	24
7/13/99	***3.98***	5.13	5.61	24
6/15/99	***3.25***	5.05	6.1	24
6/3/99	***3.26***	5.29	6.66	24
4/1/99	6.08	7.25	8.97	24
3/4/99	6.89	7.28	8.94	24
1/6/99	8.18	9.76	11.71	24
12/15/98	6.12	8.04	9.46	24
10/28/98	5.55	6.21	7.43	24
9/23/98	***3.91***	5.63	6.65	24
8/27/98	***0.29***	***1.92***	***4.23***	24
7/31/98	***1.84***	***2.71***	***3.64***	24
7/1/98	***3.33***	***4.7***	6.62	24
5/5/98	***3.25***	5.37	6.98	24
4/8/98	4.33	6.21	7.95	24
3/16/98	4.87	5.94	6.61	24
2/17/98	6.16	7.39	8.37	24
12/17/97	7.13	9.59	14.05	24
11/18/97	6.44	7.95	9.88	24
10/21/97	6.67	7.39	7.69	24
9/25/97	***3.94***	5.33	8.34	24

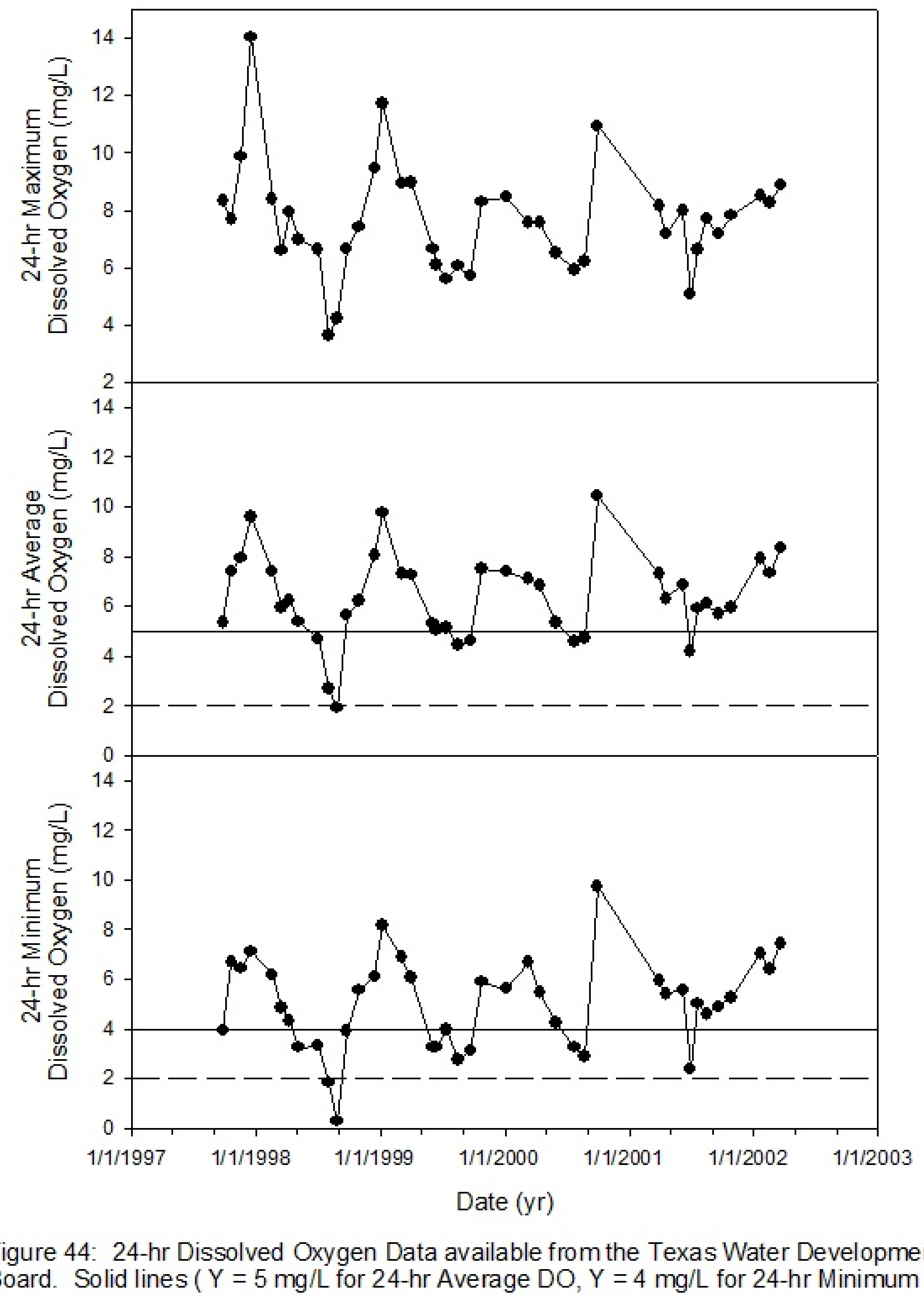


Figure 44: 24-hr Dissolved Oxygen Data available from the Texas Water Development Board. Solid lines (Y = 5 mg/L for 24-hr Average DO, Y = 4 mg/L for 24-hr Minimum DO) represent TNRCC criteria. Dashed lines are Y = 2 mg/L for hypoxia.

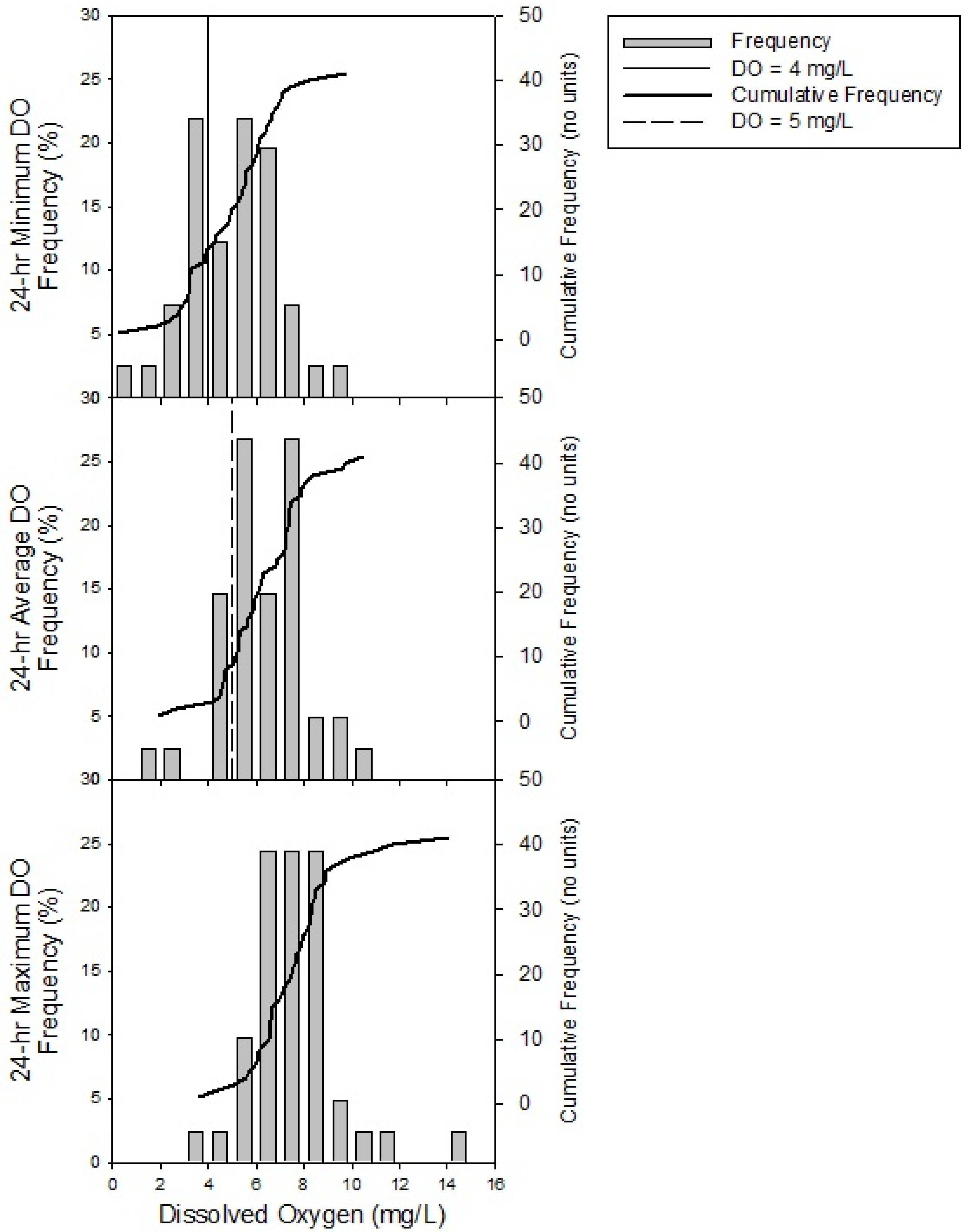


Figure 45: Frequency of the Texas Water Development Board's 24-hr dissolved oxgyen values (mg/L).

observations were in the range 3 - 7 mg/L. Eighty-three percent of 24-hr average DO observations were in the range 4 - 8 mg/L. Eighty-three percent of 24-hr maximum DO observations were in the range 4 - 9 mg/L (Fig. 45).

Discussion

Low DO (i.e., DO < 5 mg/L) appears to be a common feature in Lavaca and Chocolate Bays (Segment 2453). Of the 35 stations in Lavaca Bay analyzed for DO, there were less than 10 observations for 24 stations (Table 3). Grab-sample data for only 11 stations indicated possible low DO (i.e., < 5 mg/L; Table 3). These stations are: 12533, 12534, 13288, 13289, 13291, 13294, 13295, 13383, 13384, 13385, and 13563 (Table 3). In Lavaca Bay, 3% of TNRCC's surface DO grab-sample data were hypoxic (Fig. 8).

Although they are designated in the dataset as being within the confines of segment 2453, five of these stations (i.e., 13288, 13289, 13291, 13294, 13295) are not covered under the Lavaca Bay TMDL project because they are designated as tidal streams (i.e., tributaries to Lavaca Bay). Four of these stations had low surface water oxygen (i.e., grab-sample DO < 5 mg/L; Fig. 18), but because they lie outside the study area, they were not investigated in detail. The remaining 6 stations are: 12533, 12534, 13383, 13384, 13385, and 13563, the last four have been proposed as sampling locations in the Lavaca Bay TMDL QAPP and Field Monitoring Plan. Station 12533 was not analyzed in detail because it contained only one DO observation < 5 mg/L and no hypoxic observations.

<u>Grab-Sample Data</u>

STATION 13385

Station 13385 is described in TNRCC records as being at the Alcoa Ship Dock off the loading dock. However, the latitude and longitude of record places this station roughly 1 mile from the location TNRCC personnel say they sample. The deepest recorded depth for this station is 12.8 m. Out of 100 DO observations, 17 demonstrated hypoxia (i.e., DO < 2 mg/L). Bottom hypoxia is a recurring issue at Station 13385 and appears to be linked to water column stratification. This might be expected because Station 13385 is at the Alcoa Ship Dock, which is deep and protected, both of which could inhibit mixing of oxygenated, fresher surface water into deeper water.

STATION 13384

Station 13384 is located at the Y intersection of the Port Lavaca and Matagorda Ship Channels at CM66. The deepest depth for this station is 13.2 m, however, depth profile data for this station were done at different depths. For example depths for profiles taken prior to May 1993 ranged 9 - 12 m, whereas depths after that date were 1.2 - 4.3 m with 3 exceptions. This station is at the Y-intersection of the Port Lavaca and Matagorda Ship Channels at CM66. There are two possible explanations for the sampling disparity: 1) depth profiles were not consistently taken in the channel, or 2) TNRCC staff broke with monitoring protocol as outlined in the SWQM Procedures Manual and did not take measurements at the bottom of the channel.

Out of 128 DO observations at the station, 7 demonstrated hypoxia (i.e., DO < 2 mg/L). Salinity stratification at station 13384 ranged from slightly stratified (SigmaSal < 1 ‰) to severely stratified (SigmaSal > 20 ‰). It is unclear if the large number (30%) of low SigmaSal values

(Fig. 26) is correct for the station or if it is an artifact arising from different depths being profiled. It is possible that this station is more frequently stratified than indicated by the data.

Station 12534

Station 12534 is located in Lynn's Bayou. The deepest recorded depth for this station is 4.6 m. Out of 62 DO observations at this station, 4 demonstrated hypoxia (i.e., DO < 2 mg/L). The data that was available indicates a frequent occurrence of DO depletion despite the shallow depth. Three occurrences of hypoxia were observed in depth profiles (Fig. 29) indicating this station may warrant further investigation. Although the depth at station 12534 was < 5 ft, water column stratification was found January 1997 with a SigmaSal > 15 ‰.

Station 13383

TNRCC records describe station 13383 as being at State Highway 35. The latitude and longitude of record for station 13383 places this station at state highway 35 and the west Lavaca Bay shoreline. TNRCC personnel say that this station is sampled at the intersection of state highway 35 and the channel, approximately ½ mile from the location of record. The deepest recorded depth for this station is 9.14 m, however, the next deepest depth of record is 4.57 m indicating that the correct depth may be 4.5 m. Out of the 154 DO observations available for this station, none were hypoxic (i.e., DO < 2 mg/L). Water column stratification and concomitant DO depletion at station 13383 was not seasonally limited (Fig. 30). However, more than 40% of the SigmaSal observations were < 1 ‰ (Fig. 31) indicating that stratification was not a frequent occurrence. In spite of the shallow depth (< 4.5 m), stratification may be an important feature at this station; 2 observations had SigmaSal > 10 ‰. Although stratification occurred at station 13383, 75% of SigmaDO values were > -1 mg/L indicating the DO depletion with depth is not a frequent occurrence at this station. Further, no SigmaDO values were < -4 mg/L.

Station 13563

TNRCC records describe station 13563 as being 152 m south-southwest of CM22 in Red Bluff Channel. Station 13563 is shallow with the deepest recorded depth being 4.5 m (Fig. 34). Out of the 30 DO observations available for this station, none were hypoxic (i.e., DO < 2 mg/L). As is expected at shallow depths, stratification and concomitant DO depletion with depth were not major features at this station. Stratification was not common because more than 75% of SigmaSal values were < 1 ‰. Only 1 SigmaSal observation was > 3 ‰ indicating that stratification did not occur frequently at this station. Oxygen depletion with depth was not common because more than 75% of SigmaDO values were > -1 mg/L, and all SigmaDO observations were > -2 mg/L .

Possible Causes of Dissolved Oxygen Depletion in Lavaca Bay

Several natural factors may contribute to the depletion of DO in Lavaca Bay. The saturation concentration of DO varies inversely with temperature and salinity. In other words, when temperature and/or salinity are high, water will contain less DO than when temperature and/or salinity are low. In Lavaca Bay, surface DO (depth < 0.3 m) was lowest during summer months when temperatures peaked (Fig. 6).

Water column stratification is another natural factor that may contribute to the depletion of DO in Lavaca Bay. In estuaries, water column stratification can be induced by the influx of freshwater which overlies a layer of much saltier water (e.g., Fig. 20, February 1998; Fig. 21, November 1994; Fig. 25, May 1992, August 1993, July 1997; Fig. 29, January 1997; Fig. 30, January 1997, November 1997). Water column stratification inhibits the mixing of oxygenated surface waters to deeper waters; the larger the surface to bottom salinity difference, the more mixing is inhibited. In shallow areas, low bottom DO may not be induced because of benthic photosynthesis (e.g., benthic diatoms), however, water turbidity may inhibit DO production by photosynthesis.

Inhibition of mixing processes that give rise to water column stratification may also be caused by anthropogenic alterations to the bay, such as the presence of a man-made channel, harbor, or island. Stations 13385 and 13384 are both located in channels. Both stations have had multiple incidences of low DO (Tables 3 and 4). Depth profiles of these stations indicate stratification is common (Figs. 20, 21 and 25). Twenty percent of SigmaSal observations at stations 13385 and 13384 were greater than 10 ‰, and some observations were greater than 20 ‰ (Figs. 22 and 26). In addition to stratification, DO depletion in excess of 4 mg/L was also found at these stations (Figs. 19 and 27).

Another factor that may contribute to DO depletion in Lavaca Bay is nutrient loading. Ammonia and ortho-phosphate concentrations were higher with lower salinity (Fig. 13) indicating possible non-point source nutrient contributions to Lavaca Bay. Based on data available, it is not clear if the nutrient influx is of natural or anthropogenic origin. Nutrients contribute to DO depletion via eutrophication processes. Eutrophication can lead to increased phytoplankton production followed by increased consumer production. The wastes of this productivity (e.g., dead cells, excrement, exudates) can settle to the benthos where decomposition processes occur and microbial respiration depletes the surrounding water of DO. In some cases benthic DO can be replenished via mixing processes or benthic primary production, however, if mixing processes are inhibited by stratification or the presence of man-made structures (e.g., channels, harbors) DO may be depleted to the point of hypoxia. Eutrophication is not in itself harmful to the ecosystem; it can boost production without causing DO depletion under some conditions. Where excess nutrients are associated with low DO, nutrient controls are needed to increase DO levels.

Implications for Monitoring

The historical data review supports the original proposal to collect data at TNRCC stations 13383, 13384, 13385, and 13653 as described in the Lavaca Bay TMDL Project QAPP and Monitoring Schedule. It also uncovers the necessity of adding one additional station, TNRCC station 12534, for which several incidences of hypoxia were observed in grab-sample data.

The Lavaca Bay TMDL project requires DO data to be collected during the index period of March 15 to September 15, however, it may be informative to collect more data outside this period because TNRCC data indicates water column stratification and concomitant DO depletion is not seasonally limited (Figs. 20, 21, 25, 29, and 30). For example, salinity stratification and bottom hypoxia at station 13385, Alcoa Ship Dock, is not seasonally limited (Fig. 20 and 21).

Evaluation of Data Available for 24-hr DO Assessment

10 Measurement Requirement

According to the DO Monitoring Fact Sheet (Appendix A), a DO assessment must consist of at least 10 24-hr DO measurements taken within a two to five year period. Although not explicitly stated in the DO Fact Sheet, 10 measurements are required per assessment unit (Sandra Alvarado, personal communication, July 15, 2002). An assessment unit consists of 1 or more stations and is defined by the historical pooling of stations by the TNRCC. The DO Fact Sheet does not address how many stations are required per segment to conduct an assessment.

Historically, the TNRCC has pooled stations in Lavaca Bay into 4 groupings, called assessment units, ranging in size from 2.5 - 18.8 mi^2. The assessment units for Lavaca Bay are: Mouth of Lavaca Bay to Gallinipper Point (18 mi^2), Gallinipper Point to SH35 (15.5 mi^2), Point Comfort Area (2.5 mi^2), and Upper Bay (18.8 mi^2).

At the end of the index period in 2002, more than 10 measurements will be available for each assessment unit except the Gallinipper Point to State Highway 35 (SH35) unit which will have only 9 measurements (Table 7a). If the TWDB data is included in the assessment, a total of 34 measurements will be available for the Gallinipper Point to SH35 assessment unit, and the 10 measurement minimum will be met (Table 7a). At the end of the index period in 2003, more measurements per assessment unit will be available than in 2002 for each assessment unit, and the 10 measurement minimum will be met without inclusion of the TWDB data (Table 7b).

Critical Period Requirement

According to the DO Monitoring Fact Sheet (Appendix A), all observations considered in the assessment must be taken within the index period of March 15 to October 15. In addition, at

Table 7: Number of 24-hr DO measurements for each assessment unit that will be available for assessment of data concluding in (a) 2002 and (b) 2003. Only 5 years fo data are included in the tables. * = sonde failed for one station so there will be 4 measurements instead of the planned 5. () indicate values for which TWDB data are included; TWDB data were not collected under an TNRCC approved QAPP.

a. 2002 Assessment

Assessment Unit	Stations	Currently Available	Planned Measurements		Total
			UTMSI	TNRCC	
Mouth of Lavaca Bay to Gallinipper Point	13384	3	5	1	14
	17555		5		
Gallinipper Point to SH35	13383	3		1	9
	17554		5		(35)
	TWDB	(26)			
Point Comfort Area	13385	4	5	3	12
Upper Bay	13563			2	11
	17552		5		
	17553		4*		

b. 2003 Assessment

Assessment Unit	Stations	Currently Available	Planned Measurements			Total
			UTMSI	TNRCC	TWDB	
Mouth of Lavaca Bay to Gallinipper Point	13384	3	5	2		15
	17555		5			
Gallinipper Point to SH35	13383	3		2		10
	17554		5			(29)
	TWDB	(26)			5	
Point Comfort Area	13385	4	5	7		16
Upper Bay	13563			4		13
	17552		5			
	17553		4*			

Table 8: Assessment of historical data available for inclusion in the final assessment of dissolved oxygen in segment 2453, Lavaca Bay and Chocolate Bay. A = number of 24-hr dissolved oxygen (DO) observations for the year. B = number of 24-hr DO observations during the index period (March 15 and October 15). C = number of 24-hr DO observations during the critical period (July 1 - September 30). D = percentage of all measurements taken in one year that were taken during the critical period. NED = Not Enough Data for determination.

Begin Date	**13385**				**13384**				**13383**				**TWDB**			
	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
1998													10	7	4	57%
1999													8	6	3	50%
2000	1	1		0%	1	1		0%	1	1		0%	8	5	3	60%
2001	2	2	1	50%	2	2	1	50%	2	2	2	100%	8	7	3	43%
2002	1	1		NED									3	1		NED

least one observation, and between ½ and 2/3 of each year's samples, must be taken during the critical period between July 1- September 30.

Ten 24-hr DO observations are currently available from the TNRCC dataset, and 41 24-hr DO observations were available from the TWDB dataset for the period January 1998 to present (Table 8). All 10 TNRCC observations and 26 TWDB observations were collected during the index period yielding a total of 36 observations that can be used in the DO assessment (Table 8). However, the critical period requirement is not consistently met. The TWDB station meets the critical period requirement for years 1998, 1999, and 2000 (Table 8). Of the 10 TNRCC measurements, only 4 meet the critical period requirement (Table 8).

At the end of the 2002 index period, the critical period requirement is met for the Upper Bay and Point Comfort assessment units (Table 9a). The Mouth of Bay to Gallinipper Point assessment unit meets this criteria for years 2001 and 2002, but not for 2000 when only one measurement was taken two days prior to the critical period. The Gallinipper Point to SH35 assessment unit meets the critical period requirement for only year 2002; in 2000 and 2001, all measurements were taken during the critical period. The three measurements in 2000 were taken on June 27 and 28, only a few days before the beginning of the critical period, but will be considered as being within the critical period although they do not strictly meet the definition. Although both measurements taken at the Gallinipper Point to SH35 assessment unit in 2001 were taken during the critical period (i.e., > 2/3 of that years samples), these will be considered in the assessment as well because they are in the critical period when low DO is expected. The same critical period issues hold for a 2003 assessment (Table 9b).

Table 9: Assessment of all data anticipated to be available for inclusion in a (a) 2002 and (b) 2003 assessment of dissolved oxygen in segment 2453, Lavaca Bay and Chocolate Bay. B = number of 24-hr DO observations during the index period (March 15 and October 15). C = number of 24-hr DO observations during the critical period (July 1 - September 30). D = percentage of all measurements taken in one year that were taken during the critical period. () indicate values for which TWDB data are included; TWDB data were not collected under an TNRCC approved QAPP.

a. 2002 Assessment

Assessment Unit	1998			1999			2000			2001			2002		
	B	C	D	B	C	D	B	C	D	B	C	D	B	C	D
Mouth of Bay to Gallinipper Pt.	0	0	0	0	0	0	1	1	100%	2	1	50%	11	7	64%
Gallinipper Pt. to SH35	0 (7)	0 (4)	0 (57%)	0 (6)	0 (3)	0 (50%)	1 (6)	1 (3)	100% (50%)	2 (9)	2 (5)	100% (56%)	6	4	67%
Point Comfort Area	00		0	0 0	0	1	1		100%	2 1		50%	9 5		56%
Upper Bay	0	0	0	0	0	0	0	0	0	0	0	0	11	6	60%

b. 2003 Assessment

Assessment Unit	1999			2000			2001			2002			2003		
	B	C	D	B	C	D	B	C	D	B	C	D	B	C	D
Mouth of Bay to Gallinipper Pt.	0	0	0	1	1	100%	2	1	50%	11	7	64%	1	NA	NA
Gallinipper Pt. to SH35	0 (6)	0 (3)	0 (50%)	1 (6)	1 (3)	100% (50%)	2 (9)	2 (5)	100% (56%)	6	4	67%	1	NA	NA
Point Comfort Area	0	0	0	1	1	100%	2	1	50%	9	5	56%	4	NA	NA
Upper Bay	0	0	0	0	0	0	0	0	0	11	6	60%	2	NA	NA

Table 10: Number of 24-hr DO measurements taken in each assessment unit each year (N) and the percentage of the total number of measurements taken over a 5-yr period taken in a given year (%) for (a) 2002 assessment, and (b) 2003 assessment.

a. 2002 Assessment

Assessment Unit	1998		1999		2000		2001		2002		Total
	N	%	N	%	N	%	N	%	N	%	
Mouth of Bay to Gallinipper Pt.	0	0	0	0	1	7%	2	14%	11	79%	14
Gallinipper Pt. to SH35	0 (7)	0 (20%)	0 (6)	0 (17%)	1 (6)	11% (17%)	2 (9)	22% (26%)	6 (7)	66% (20%)	9 (35)
Point Comfort Area	0	0	0	0	1	8%	2	17%	6	75%	9
Upper Bay	0	0	0	0	0	0	0	0	11	100%	11

b. 2003 Assessment

Assessment Unit	1999		2000		2001		2002		2003		Total
	N	%	N	%	N	%	N	%	N	%	
Mouth of Bay to Gallinipper Pt.	0	0	1	7%	2	13%	11	73%	1	7%	15
Gallinipper Pt. to SH35	0 (6)	0 (18%)	1 (6)	10% (18%)	2 (9)	20% (26%)	6 (7)	60% (20%)	1 (6)	10% (18%)	10 (34)
Point Comfort Area	0	0	1	6%	2	13%	9	56%	4	25	16
Upper Bay	0	0	0	0	0	0	11	85%	2	15%	13

Annual Sampling Requirement

The DO Monitoring Fact Sheet states: "No more than 2/3 of the samples should be taken in the same year." For a 2002 assessment, this requirement is exceeded for 3 of the 4 assessment units (Table 10a). For a 2003 assessment, this requirement is exceeded for 2 of the 4 assessment units (Table 10b). In the Upper Bay assessment unit, all measurements will have been taken during 2002 (Table 10a) for a 2002 assessment, and 85% will have been taken during 2002 for a 2003 assessment (Table 10b). The lack of annual data for the Upper Bay unit is not of great concern because it is a region where low oxygen is not expected. Although annual sampling requirement is not strictly met, all data will be considered in an assessment because they are the only data available at this time and the requirement is loosely stated (i.e., "should").

Monthly Sampling Event Requirement

The DO Monitoring Fact Sheet states: "Sampling events should be more than one month apart." Data from each source, TNRCC, TWDB and UTMSI are one or more months apart, but when this data is combined, monthly sampling is duplicated to some extent. The purpose of this requirement is to prevent numerous sampling events from occurring during a short span of time and thereby unduly biasing an assessment. Although data is duplicated for some months, duplicates appear to be distributed across the index period. Further, the duplication within months occurs at different locations within the assessment unit and will provide a more spatially integrated analysis.

Sonde Depth Requirement

The DO Monitoring Fact Sheet states that sondes are to be deployed "...between a depth of 1 foot and a depth of ½ the mixed surface layer." Assuming that Lavaca Bay is well mixed because it is shallow and subjected to tidal and wind mixing forces, all samples must be taken within a depth of 1 ft and ½ the total depth of the station. This requirement is met for all data.

Measurement Interval Requirement

The DO Monitoring Fact Sheet requires that sondes record data at least once per hour and no more frequently than every 15 minutes. This requirement is met for all data.

Duplicate Sonde Requirement

According to the 24-hr DO Monitoring Fact Sheet, two sondes are to be deployed in the same general area at least 20% of the time to check for how spatially variable conditions are at deployment sites. To date, no duplicate sonde deployments have been conducted by either the TNRCC or TWDB, even with stations being pooled into assessment units. At the end of the Lavaca Bay TMDL Project Phase 1, duplicate sondes will have been deployed at stations 17552, 17553, 17554, 17555, 13384, and 13385.

Other QA Requirements

All QA Requirements have been met for data collected by UTMSI. It is not presently known to what extent TWDB data meet the QA requirements because no TNRCC approved QAPP presently exists for this data.

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Appendix A

24-Hour DO Monitoring
Fact Sheet

Index period for sampling:	March 15 - October 15. All sampling events must occur within the index period. However, at least one sample and between half and two thirds of each year's samples must be taken during the critical period of July 1 - September 30. No more than 2/3 of the samples should be taken in the same year. Sampling events should be more than one month apart. A total of ten 24-hour measurements within a two to five year period is required to provide assessment of the aquatic life use. For perennial streams, in order to determine criteria support, all ten measurements must be at or above the 7Q2, so more than ten sample-collection events may be needed. The 7Q2 for classified segments is listed in Appendix B of the TSWQS. For unclassified waterbodies, contact Suzanne Vargas: svargas@tnrcc.state.tx.us; (512) 239-4619, of the Modeling and Assessment Team to determine 7Q2. To avoid collecting samples below the 7Q2, it is recommended that flow be determined before beginning a 24-hr sampling run.
Depth on streams, reservoirs, or estuaries:	Deploy sonde at a point between a depth of 1 foot and a depth of ½ the mixed surface layer.
How often to record:	Measurement interval should be no more frequently than once per 15 minutes and no less than once per hour. Four or more dissolved oxygen measurements may also be made manually at even intervals over one 24-hour period at a site, as long as one is made near sunrise to approximate the daily minimum.
Data reporting:	Parameter Codes • 24-hour averages DO: **89857**; temperature: **00209**; specific conductance: **00212**; pH n/a • # of measurements over a 24-hour period: **89858** • Minimum values DO: **89855**; temperature: **00211**; specific conductance: **00214**; pH: **00216** • Maximum values DO: **89856**; temperature: **00210**; specific conductance: **00213**; pH: **00215** Program Codes • Diel sampling (multiple field measurements conducted over a 24 hr period and/or summary 24 hr D.O. statistics), not conducted under the scope of a TMDL QAPP: **DI** • Diel sampling conducted under the scope of a TMDL QAPP: **TI**
QA requirements:	• If sampling is multiday, the measurement (average) used for the assessment will be the first 24-hour period recorded during the deployment. Following multiday deployments, evaluate and report only creditable data (free from drift). • During initial multiday sampling, drift must be checked each day with a recently calibrated separate instrument, until it is known how long the multiprobe can be deployed before significant drift occurs. • Reference checking of the multiprobe will generally be required at 3- 7 day intervals. • When setting up a YSI, ensure that the warm up time is set at 90 seconds, rather than the instrument default. • Twenty percent of the time, deploy two sondes in the same general area as a test of how spatially variable conditions are at deployment sites. This QA check may be revised after we have gained some experience.
When to collect other routine field measurements and water samples:	Should collect at either the time of deployment, reference check, or retrieval of 24-hour monitoring multiprobe. Flow must be measured at site unless it is not possible to do so.
Priority for scheduling 24-hour sampling:	1. 303d listed waterbodies 2. Waterbodies with Concerns for DO problems (too few samples available for full use assessment). 3. Occurrence of low DO concentrations observed during the day 4. Waterbodies with trends indicating declining concentrations 5. Waterbodies which would contribute to Ecoregion data set